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Characterization of Crystallizable Polybutadiene Blends

by

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Abstract: This report discusses the characterization of binary blends of 1,4 trans and 1,2 syndiotactic polybutadienes of various compositions. The blends were prepared by solution precipitation and analyzed by means of differential scanning calorimetry, Rheovibron viscoelastometer, wide angle X-ray scattering (WAXS), and light microscopy. The blends were not isomorphic. The melting point (T_m) and glass transition (T_g) of the trans component were affected to a greater degree by the presence of the syndio component than the syndio T_m and T_g values were affected by the trans component.

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INTRODUCTION

This progress report describes work done between April and October, 1988, on the topic "Blends of Crystallizable Polybutadienes: Morphology Control via Diblock Addition in the Melt." The overall objectives of the research are to determine a) the compatibility and behavior of binary blends of crystallizable syndiotactic 1,2 and trans 1,4 polybutadienes (PBD) and b) the effect of amorphous 1,2/1,4 PBD diblocks on the phase separation of these blends in the melt and the subsequent solid-state structure and properties of these copolymer-modified blends.

Earlier work on this topic focused on preliminary characterization of the individual homopolymers and of 50/50 (weight% syndio / weight% trans) blends of the homopolymers and is documented in a previous ONR report (Marx and Cohen, 1988). That report summarized IR, NMR, and DSC data for the homopolymers and discussed optimization of a spincasting technique used to obtain polymer films. It also presented DSC data for the homopolymers and 50/50 blends for samples obtained through spincasting.

The current report discusses polymer precipitation followed by compression molding as a preferred method for obtaining films. This report also documents extensive characterization of the homopolymers and of 5/95, 25/75, 50/50, 75/25, and 95/5 binary blends. Specifically, results of Rheovibron, WAXS, DSC crystallization, and light microscopy melt studies are presented and discussed here for samples prepared by the precipation/press-molding technique.

SAMPLE PREPARATION

Polymer films are needed for Rheovibron, X-ray, and mechanical spectrometry experiments and can be used for microscopy. Precipitation followed by compression molding was examined as an alternative to the spin-casting method of preparing sample films due to a number of problems that arise with the latter technique.

With spincasting (described in the previous ONR report mentioned above), the polymer films stuck to the mylar insert and made it difficult to remove the films without damaging them. Degradation was minimized by blowing 10 SCFH of nitrogen through the casting cup, but there was still a distinct color difference between the starting materials and the ending films. Complete solvent removal was difficult because tetralin, the casting solvent, has a high boiling point of 209°C and consequently a relatively low vapor pressure. Also, sample thickness was

limited because initial polymer solutions were difficult to work with at concentrations greater than 2%.

Precipitation of Polymers in Methanol

Our polymers readily go into solution in tetralin at temperatures above 120°C for trans and above 140°C for syndio. As an alternative to spincasting, the hot solutions are precipitated by dripping them into methanol. The precipitated polymer is then easily filtered and dried in a vacuum oven. This method is advantageous for a number of reasons: a) it is much more straight forward than spin-casting, b) tetralin removal is easier because it is soluble in the methanol thus the tetralin that dissolves in the methanol can be separated from the polymer by filtration, c) given enough material, films can be pressed into any desired shape and thickness. One drawback is that methanol's flash point is 11°C (52°F) thus care must be taken to keep the methanol below this temperature when the hot tetralin solution is poured into the methanol. This safety precaution is easily accomplished by stirring the beaker of methanol inside a bucket of dry ice and by slowly dripping the solution into the methanol. It is important to drip the hot solution slowly into the stirred methanol for another reason: if the precipitate is not composed of small, flaky-like particles, the resulting dried polymer will not mold well and will yield discolored degraded films that are not uniform in thickness.

We generally prepare batches of 1 gram of precipitated polymer. The polymer or polymer blend and 0.01 grams of Irganox 1076 antioxidant are gently stirred in 50ml of tetralin at ~150°C-180°C for at least one half hour. This solution is then dripped into ~300 ml of methanol and filtered through analytical paper (we use Schleicher and Schuell type #595) in a buchner funnel. The damp polymer is then vacuum dried at a temperature <70°C for about 1.5-2 weeks, or until the sample achieves constant weight. Generally, there is still a faint solvent smell remaining after 2 weeks in the oven, but subsequent drying does not remove any measurable amount of solvent.

Our homopolymers are sensitive to oxidative degradation at high temperatures. In earlier spincasting optimization experiments, high flows of nitrogen in the spincasting cup (10 SCFH vs. 1.0 SCFH) greatly reduced the degree of film discoloration. Thus, the optimal situation is to work in an oxygen-free environment when preparing or testing our polybutadiene samples.

Evaluation of Antioxidants

For processes where it is difficult to create an oxygen-free or oxygen-reduced atmosphere, antioxidants are often helpful in eliminating or at least delaying degradation. Three

antioxidants were tested for effectiveness at a concentration of 1% per gram of polymer. Testing was accomplished by adding the antioxidant to both 1% syndio and 1% trans solutions in tetralin. The solutions were precipitated in cold methanol, as discussed above, and the polymer filtrate was dried to constant weight. All samples, including controls without antioxidant, were subjected to DSC testing to determine the onset of degradation. In a second set of syndio tests, the above experiment was repeated for the the two most effective antioxidants and additional samples were tested for which the antioxidants were added not only to the polymer solution but also to the methanol in a concentration of ~1% antioxidant per gram methanol. This amount of antioxidant resulted in a saturated methanol solution and excess antioxidant that precipitated out of the cold methanol.

The antioxidants tested were Ethanox 330 (Ethyl Corp.), Irganox 1076 (Ciba-Geigy Corp.) and Wytox HPM (Olin Chemicals). These products were chosen upon recommendation of the manufacturers for high temperature stabilization of polybutadienes and based on their melting and decomposition temperatures. Further information concerning the antioxidants is as follows:

Ethanox 330 is a substituted phenol with a melting point of 244°C. The chemical name is 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxy-benzyl) benzene.

Irganox 1076 has a melting temperature of 50-55°C and a decomposition temperature >220°C. Its chemical name is octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate.

Wytox HPM is a hindered phenolic product with a melting point of 245-255°C. Its chemical name is bis-2,2-methylene bis(6-t-butyl-4 methyl phenyl)terephthalate.

Results of the DSC testing are tabulated in Table 1. For a given test, the melting points are reproducible. The onset of degradation was taken to be the temperature where the slope of the DSC curve started to become negative given a straight baseline. The results show that trans degrades at about 230°C without antioxidant and syndio at about 210°C. In the first set of tests, Irganox 1076 delayed degradation most effectively for the trans (about 25°C) while it had no effect for the syndio. Ethanox 330 delayed degradation by about 10°C for both polymers. Wytox HPM did not help either homopolymer. In the second set of tests, where Irganox 1076 and Ethanox 330 were retested with syndio and additionally put into the methanol, Ethanox 330 did not have a significant effect but Irganox 1076 was more effective than previously observed. However, with 1% antioxidant per gram of methanol, the amount of Irganox 1076 in the final dry polymer

sample listed in table I was greater than 50% of the total weight and lowered the syndio melting point by 20°C!

In summary, Wytox HPM had no apparent affect, and Irganox 1076 was more advantageous than Ethanox 330 in almost all cases. For this reason, Irganox 1076 is the preferred antioxidant in concentrations of 1% antioxidant per gram polymer. The results also suggest that antioxidant in the methanol is desirable, but in concentration low enough to prevent melting point alteration due to excess antioxidant. Thus only 0.01% antioxidant per gram methanol (or about 2-3X the amount in the tetralin solution), in addition to the 1% per gram polymer in the tetralin solution, was chosen as an appropriate amount for subsequent precipitation preparations.

Compression Molding

To make films, 0.5g of precipitated, dried polymer powder is placed in a copper mold of dimensions 0.5 inches x 2.5 inches x 0.02 inches and pressed in a preheated laboratory press (Carver, 11 metric ton capacity) at a temperature of 200-205°C and a pressure of 3 tons for 2.75 minutes. Upon reaching 2.75 minutes, the pressure is released, and the mold is removed from the press and allowed to cool at room temperature. When the mold is cool enough to be handled without gloves, the top and bottom plates are separated and the film is carefully removed and stored away from light until further use. Before each molding cycle, all surfaces of the mold are sprayed with Flouroglide (Norton Company, Wayne, NJ) to ensure easy film removal at the end of the molding process.

The effects of precipitation and molding on molecular structure have been checked using high temperature ^{13}C and ^{1}H NMR on 2% solutions of syndio and trans samples. The NMR spectra reveal no noticeable bonding changes for samples that have undergone the precipitation and molding process described above.

In summary, a successful precipitation and molding technique has been developed to prepare polybutadiene blends. Of three antioxidants tested, Irganox 1076 seems to be the most effective for both syndio and trans polybutadiene, and it delays the onset of degradation by 10°-20°C when samples are heated at a rate of 20°C/minute in the DSC.

HOMOPOLYMER AND BLEND CHARACTERIZATION BELOW MELT TRANSITION

Previously, IR, NMR, and melting point data were collected for trans and syndio homopolymers, both of which have a molecular weight of about 250,000 g/mol. For trans, $M_w/M_n=2.3$ (Halasa, 1988), for syndio the polydispersity is unknown. Since the previous report, we have performed an Avrami analysis on the

homopolymers and crystallization studies on various binary blends. Also, the optimization of film preparation has facilitated the use of Rheovibron and WAXS experiments to obtain additional information for the homopolymers and blends.

Avrami Analysis

Precipitated, unmolded homopolymer powders were subjected to Avrami analysis. Samples were heated above their melting point at a rate of 20°C/min and then cooled at 2°C/min until crystallization was completed. In one set of samples the trans had a melting point of 132.6°C and crystallization occurred from 120° to 115°C, corresponding to an undercooling of 12.6°C for the onset of crystallization. For syndio, the melting point was 184.4°C and crystallization occurred from 162° and 151.4°C, corresponding to an undercooling of 24.4°C. To obtain data for the Avrami analysis, syndio samples were heated at a rate of 200°C/min to 205°C, held at this temperature for 1 minute, cooled at 200°C/min to 156.5°C, held at this temperature for ~10 minutes (or until the scan line returned to the original baseline) and then cooled at 200°C/min back to room temperature. Another syndio trial was performed with an isothermal crystallization temperature of 160°C. Similarly, two trans samples were heated at 200°C/min to 150°C, held 1 minute, cooled at 200°C/min to 117.8 and 120°C, respectively, and held isothermally until crystallization was complete.

A second set of syndio and trans samples was tested to obtain additional data and verify the previous results. In this set of samples, the syndio had a melting point of 188.3°C and crystallized from 164° to 150°C, giving an undercooling of 24.3°C as with the previous syndio sample. The trans had a melting point of 132.5°C and crystallized from 119.5° to 111.5°C, corresponding to an undercooling of 13°C, which is also consistent with that for the previous trans sample. Here, three syndio samples were held isothermally at 158°C, 163°C, and 164.5°C. Three trans samples were held isothermally at 116°C, 119°C, and 120.5°C. For these syndio and trans samples, precipitation had taken place in the presence of antioxidant; for the first set of samples, no antioxidant was used in the preparation.

According to Avrami (1940), isothermal crystallization is related to time by the expression $X_c = 1-\exp(-kt^n)$ where X_c is the degree of crystallinity at time t relative to the crystallinity of the sample at infinite time, k is the bulk crystallization rate constant, and n is the Avrami exponent. A log-log plot of $-\ln(1-X_c)$ vs t then yields a y-axis intercept of log k that corresponds to t=1 minute. The slope of the plot is n.

By taking ten equal time increments along each crystallization curve, X_c as a function of time was calculated as the ratio of the area under the curve at a given time increment relative to the total area for the crystallization process. Instrument-based transients in the DSC scans were removed by extrapolation back to the position where the temperature reached the isothermal setpoint.

X_c versus time curves are shown in Figure 1. The log-log plots are shown in Figure 2, and k and n values are listed in Table 2. Because the plots are not linear but exhibit a decrease in slope with time, k(avg) and n(avg) values in Table 2 are an average of the two values obtained from: a) the line composed of the data points from the three shortest time measurements and b) the line composed of the data points of the five longest time measurements from the curves in Figure 2. This decrease in nucleation rate is indicative of secondary crystallization of amorphous material as nuclei are exhausted during thermal heterogeneous nucleation (Wunderlich, 1976). Yagpharov (1986) argues that secondary crystallization is independent of primary crystallization and leads to "fringed micelle" crystal formations. Wunderlich remarks that crystal perfection after impingement of the initial crystal formations also contributes to this decrease in slope with time but also warns that the Avrami expression is not applicable to crystal perfection.

Our values of n for syndio at short times (i.e. during primary crystallization) are 4.7-5.9 and at long times are 1.4-3.3. Obata et al. (1975) report n values of 3.1-3.3 for syndio with an overall crystallinity of 25% and n values of 2.6-3.5 for syndio with an overall crystallinity of 46%. For trans, we obtained n values of 3.7-6.7 for primary crystallization and 1.5-2.9 for long times. Bermudez et al. (1970) report n to be 2.2±0.4 for trans PBD, which agrees with the average value of n reported here for secondary crystallization in trans.

For spherulitic growth with heterogeneous (also known as predetermined or athermal) nucleation, n=3. For homogeneous (or sporadic or thermal) nucleation, n=4 (Meares, 1965; Wunderlich, 1973). In light microscopy experiments, we have not seen spherulitic structures and work is in progress to determine the crystal morphology of our homopolymers. Without additional information on nucleation and morphology, it is difficult to interpret our n values, but the parameters we have derived here allow us to conveniently represent crystallization data for trans and syndio PBD homopolymers.

A plot of k(avg) versus degree of undercooling is shown in Figure 3 for both syndio and trans. For all samples, the k values increase exponentially with degree of undercooling due to the increased driving force for crystallization at lower temperatures. If the crystallization temperatures were to

approach much closer to T_g, we would expect k values to level off and finally decrease since crystallization is then hindered by transport limitations as the polymer becomes glassy. The smaller degree of undercooling needed for trans crystallization probably indicates that trans requires a smaller activation energy than syndio for crystallization. One explanation for this occurrence is that trans may be ordered to a higher degree in the melt than syndio and thus crystallizes with a lower activation energy.

Despite limitations of Avrami analysis, we have learned where to expect component crystallization. In the temperature range 125°C-155°C, a binary blend of our homopolymers is expected to be composed of crystallized syndio and melted trans. For relatively short times, blends cooled to 165°C are expected to be totally in the melt phase, while at 110°C both components should have already crystallized.

DSC Crystallization Studies

DSC studies were performed on a series of binary blends to determine the effects of isothermal crystallization at various temperatures on subsequent melting.
Specifically, binary blends of five compositions were heated in powder form to the melt state (205°C), held at that temperature for one minute, quenched at 200°C/min to one of six temperatures, held at that temperature for two minutes, and then quenched down to room temperature at a rate of 200°C/min. After an additional five minutes at room temperature, the samples were scanned at a heating rate of 20°C/min to determine melting (or transition) points and associated enthalpies.

Indium standards were run on the DSC with every use and showed that day-to-day reproducibility can vary by as much as 1.2°C. The lowest melting point obtained for indium heated at 20°C/minute was 160.5°C. When the DSC gave an indium melting point above this value, all subsequent temperature measurements taken at a heating rate of 20°C/minute were corrected by an amount equal to the difference between the observed indium melting point and 160.5°C.

The five blend compositions tested here were 5/95, 25/75, 50/50, 75/25, and 95/5. Precipitated homopolymers were also tested. The isothermal crystallization temperatures were 165°C, 155°C, 140°C, 125°C, 110°C, and 25°C. These temperatures were chosen because they represent, respectively, just above the syndio crystallization point, just below the syndio crystallization point, midway between syndio and trans crystallization bounds, just above the trans crystallization point, just below the trans crystallization point, and room temperature. A complete set of blends was also scanned directly, i.e. without any imposed thermal history other than that incurred during precipitation.

Table 3 lists results for all of these trials. Melting points of the two components (T_s and T_{tII}) and the trans crystal-crystal transition temperature (T_{tI}) are listed; enthalpies for these transitions are listed both as absolute amounts (H_s, H_{tI}, and H_{tII}) and as percentages relative to homopolymer enthalpies ($\%H_s$, $\%H_{tI}$, and $\%H_{tII}$). Graphs of melting temperatures and %enthalpies as a function of syndio composition for the isothermally crystallized samples are presented in Figure 4 for the 165°C and 140°C trials and in Figures 5 and 6 for all trials.

Repeat trials at 140°C for the 5/95 blend in Table 3 show that enthalpy and temperature values for the same test can vary by 0.7 cal/g and 1.6°C, respectively.

For melting points and T_{tI} values, in Figure 4a there is no significant difference between results for 165°C and 140°C trials and when plotted on this scale, there is little discernable effect of blend composition. Considering all of the results for various isothermal crystallization temperatures shown in the expanded plots of Figure 5, no trend is apparent in the melting temperatures with regard to varying the crystallization temperature. Concerning blend composition in Figure 5, at 50% and 95% of either component, the melting temperatures for that component are greater than those for blends of any other composition. This phenomenon gives the graphs in Figure 5 a zig-zag look. Also, 5% blends of either component always give lower melting points than the corresponding homopolymer melting point. At 5% trans, the melting point is lowered by 9°C relative to 100% trans, and the difference between 5% and 100% syndio is about 2°C. Polymer melting point depression in the presence of a diluent is discussed by Flory (1953) and is related to the classical melting point depression characteristic of a pure substance in the presence of a diluent. The fact that the depression here is small for both components indicates that they primarily crystallize independently of each other but are affected by the presence of the other to a slight degree, with the trans component affected to a greater degree than the syndio.

Regarding enthalpies, Figure 4b shows percent enthalpy relative to homopolymer enthalpy at that test temperature for 165°C and 140°C trials. For all syndio compositions, the $\%H_s$ at a given composition is always greater than that composition. The dash-dot line in Figure 4b represents $\%H_s$ equal to %syndio. For both forms of trans, at compositions greater than 75%, $\%H_t$ values are greater than the corresponding composition, but below 50% trans the $\%H_t$ values are lower than their corresponding compositions. The dashed line depicts $\%H_t$ equal to %trans. These results, coupled with the overall melting point depression data mentioned above and rheovibron data to be discussed later in this report, show that trans crystallization is adversely

affected by the presence of the syndio to a greater degree than the syndio is affected by the presence of the trans. But in all cases, these deviations from simple additivity of enthalpy are small.

The results of this study definitively show us that two melting points appear in every scan of a blend, and thus demonstrate that our blend is not isomorphic. For a blend to be isomorphic, it must have only one melting point for every composition with the value of the melting point intermediate between the melting points of the homopolymers that comprise the blend. As a first approximation, these binary blends appear to behave as simple heterogeneous mixtures of the two semicrystalline components with little interaction between the two components.

One final observation is that for all samples with syndio content 25% and above that underwent crystallization at temperatures of 125°C and above, a small peak appeared in the DSC heating scans at a position about 5°-10°C above the isothermal crystallization temperature. This phenomena was observed by Ashitaka et al. (1983) and Obata et al. (1975) for syndio and by Yagpharov (1986) for PDMS, PET, and polyurethane and is due to secondary crystallization, which was discussed earlier in this report. In our case, these small peaks correspond to secondary crystallization of the syndio component. The smaller the concentration of syndio or the lower the crystallization temperature, the smaller the secondary peak, thus we did not observe this peak in trials with crystallization temperatures below 125°C and for syndio compositions below 25%. Secondary crystallization peaks for the trans component were not discernable.

To summarize the results of the DSC crystallization studies, we found that:

1) two melting transitions were present in every DSC scan of a blend, thus our polymers do not form isomorphic blends.

2) the isothermal crystallization temperature did not significantly affect subsequent melting points and enthalpies for a given blend composition.

3) compared to the melting points of the respective homopolymers, there was a 9°C melting point depression of the trans component in the 95/5 blend, and a 2°C melting point depression of the syndio component in the 5/95 blend.

4) %enthalpies of the components as a function of blend composition showed that trans crystallization was mildly and adversely affected by the presence of syndio while the syndio crystallization was essentially unaffected by the presence of the

trans. This result was further substantiated by rheovibron T_g data to be discussed in the next section of this report.

5) samples with no induced crystallization history had higher absolute enthalpies (per gram of component) than the corresponding blends that were melted and recrystallized, indicating that crystallization was more complete for samples simply precipitated from solution.

6) small peaks appeared on some of the DSC scans at a temperature 5°-10°C above the crystallization temperature. These peaks are indicative of secondary crystallization of the syndio component.

Rheovibron Tests for T_g Determination

Using a Rheovibron DDC-II-C (Toyo-Baldwin Co.), data were obtained for all of the blends and homopolymer samples mentioned above in the crystallization study. Since films are needed for this instrument, precipitated, dried powders were molded to a thickness of about 0.5 mm and cut to a length and width of about 40mm x 3 mm. Unprecipitated homopolymer powders were also pressed, tested and compared with precipitated, pressed powders to examine the effects, if any, of precipitation on mechanical properties. Most samples were heated from -120°C to a temperature just below complete melting at a rate of about 2-4°C/min. PET controls were also tested to check the performance of the equipment.

Tan δ , log G' and log G" are plotted as a function of temperature in Figure 7 for unprecipitated homopolymers and in Figure 8 for precipitated homopolymers and blends. Table 4 lists approximate transition temperatures observed in the trials illustrated by Figures 7 and 8 as well as for trials not presented graphically. In Table 4, we have assigned thermal transitions to be the onset of any noticeable increase in the slope of the tan δ curve. The onset of such an increase in slope is taken to be the extrapolation of the steepest part of the curve to the baseline. Two PET controls gave reproducible T_g values of 90°C.

Regarding the homopolymers, unprecipitated 100% syndio samples gave T_g values of 20°-25° while precipitated syndio gave a T_g of 35°C. Trans samples gave T_g values of -85°C and -80°C for unprecipitated and precipitated powders, respectively. Additionally, trans samples, whether precipitated or unprecipitated, gave transitions at 70-80°C which corresponds to the crystal-crystal transition (T_{tII}) characteristic of trans. Unprecipitated syndio samples were tested to temperatures high enough to show the onset of melting at 185°-190°C.

With respect to the blends, transitions were observed for the 5/95 blend at -85°C, 85°C, and 140°C; the first peak

apparently marks trans T_g, the second is trans modI, and the third is the onset of trans melting. No peaks are present for syndio transitions but the values of log G' and log G" at any given temperature are somewhat between those of trans and syndio homopolymers. For the 25/75 blend, transitions occur at -70°C, 30°C, 85o, and 130°C, corresponding to trans T_g, syndio T_g, trans mod I, and trans melt. At this composition, the transitions are distinct in the tan δ plots and the values of the plotted variables and the shapes of the overall curves are more strongly influenced by the presence of the syndio component than they were in the plots for 5% syndio. With the 50/50 blend, transitions are apparent at -60°C, 20°C, and 135°C, corresponding to trans T_g, syndio T_g, and trans melt. The tan δ graph here appears much more syndio-like compared to the previous samples. Note also that the T_g for trans seems to be shifting higher with increasing syndio content. For the 75/25 blend, transitions appear at-50°C, 25°C, and 125°C, corresponding to trans T_g, syndio T_g, and trans melting. Although no other obvious transitions can be determined for the trans component and the shape of the plots is predominantly syndio-like, inspection of the curves at this composition shows that their shapes and the values of tan δ, log G", and log G' are still obviously influenced by the trans component. With the 95/5 blend, transitions occur at 25°C and 185°C, corresponding to syndio T_g and melting: here, no effect of the trans component is apparent to the eye.

Ashitaka (1983) reports a syndio T_g of 40°C, based on the peak of the tan δ rheovibron curve. For 94% trans, Dainton (1962) gives a T_g of -83°C determined via heat capacity measurements.

Rheovibron data of binary blends show that the blends have distinct characteristics of both homopolymers. There are obviously two glass transitions in the 25/75, 50/50, and 75/25 blends. The appearance of two glass transitions in these blends indicates that the amorphous components of the blends are mechanically distinct from each other, i.e. a single homogeneous trans/syndio amorphous phase does not exist.

The effects of the two components on each other can be observed from our rheovibron data and are quite interesting. In the 5/95 blend, the mechanical behavior is predominantly trans yet is noticeably influenced by the syndio component since the T_g is shifted higher, whereas the 95/5 sample is not noticeably different from the syndio homopolymer. As syndio content increases from 5% in the 5/95 blend to 75% in the 75/25 blend, the trans T_g tends to move higher. This situation is consistent with the DSC results in which the %enthalpy of the trans component in blends with low trans contents was lower than the corresponding %trans in the blend. Similarly, the fact that the syndio T_g remains relatively constant despite the trans content in the blend is consistent with DSC results that showed that the

%enthalpy of the syndio component was approximately equal to the corresponding %syndio in the blend. In other words, trans is more sensitive to the presence of syndio than vice-versa as far as relative enthalpy and T_g are concerned. This observation may indicate that overall syndio crystallization is unaffected by the trans yet some syndio portions mix to a small extent with the still uncrystallized trans to both lower the resulting trans crystalline enthalpy and simultaneously raise the trans T_g.

Wide Angle X-ray Scattering (WAXS)

WAXS 2θ spectra were taken on a Rigaku X-ray DIffractometer System with rotating anode and point focus for all samples tested on the Rheovibron. Spectra were also obtained for a degraded syndio sample that had a strong brown discoloration, a mixed cis/trans sample (Polysciences, 36% cis, 55% trans, 9% vinyl, MW=200,000, M_w/M_n=2.1) and cis 1,4 samples (Goodyear, 99% cis, MW=250,000, M_w/M_n=1.9-2.2; also, Polysciences, 98% cis, MW=400,000, M_w/M_n=4.0-4.5). Samples were scanned continously at a rate of 5°/min. Selected WAXS scans are presented in Figures 9-11, where Figure 9 shows homopolymer scans, Figure 10 shows blend scans, and Figure 11 depicts scans of the amorphous 1,4 samples. Representative peak positions and the corresponding d-spacings and plane assignments are summarized in Table 5a. The d-spacings were calculated using Bragg's Law:

$$d = \lambda/(2\sin\theta).$$

Miller indices were assigned using the equations listed by Cullity (1978) for orthorhombic and hexagonal cells, with orthorhombic cell dimensions of a=10.98Å, b=6.6Å and c=5.14Å for syndio (Natta and Corradini, 1956), and hexagonal cell dimensions of a=4.54Å, c=4.92Å for trans modI (Natta and Corradini, 1959). Trans modI cell dimensions of a=4.6Å, c=4.83Å reported by Suehiro and Takayanagi (1970) gave the same assignments as Natta and Corradini's trans unit cell dimensions. A summary of unit cell dimensions reported in the literature are presented in Table 5b. The equations from Cullity are

$1/d^2 = (4/3)(h^2+hk+k^2)/a^2 + l^2/c^2$ for hexagonal cells and
$1/d^2 = (h^2/a^2 + k^2/b^2 + l^2/c^2)$ for orthorhombic cells.

Using average results from all precipitated/molded samples containing syndio, including blends but excluding degraded syndio samples, peaks appeared at 2θ values of 13.4°, 16.1°, 21.1°, 23.4°, 28.0°, 31.6°, and 35.9°. These peaks correspond to d spacings of 6.6Å, 5.5Å, 4.2Å, 3.8Å, 3.2Å, 2.8Å, and 2.5Å, respectively. The peak corresponding to the 2.8Å spacing was small and did not appear in all spectra. Trans peaks for precipitated/molded samples appeared at 22.4° and 39.1°, which translate to d-spacings of 4.0Å and 2.3Å.

Natta and Corradini (1956) reported four primary peaks from X-ray data for syndio that correspond to d-spacings of 6.6Å, 5.5Å, 4.2Å, and 3.8Å, which are identical to those we have reported here. Bermudez and Fatou (1972) observed a trans peak at 2θ=22.5°C for the (100) reflection. Iwayanagi et al. (1968) and Natta et al. (1962) reported a trans peak at 22.6°. These values are effectively the same as the 2θ value of 22.4°C that we observed.

Specta of amorphous cis and mixed cis and trans samples are presented in Figure 11. These data were obtained for background information required for crystallinity calculations for the 1,4 trans samples and to check if there is a difference between high cis samples and mixed cis and trans samples. In both cis samples and in the mixed 1,4 sample (Figures 11a, 11b, and 11d), a broad peak is centered at a 2θ value of approximately 19.6°, which corresponds to an average d-spacing of 4.5Å. Scans of the amorphous samples were taken from 2θ=5° to 2θ=45°.

The degraded syndio sample gave peaks that correspond to d-spacings of 6.5Å, 5.4Å, 4.2Å, 3.8Å, 3.2Å, and 2.5Å, while unprecipitated/molded syndio samples led to d-spacings of 6.6Å, 5.5Å, 4.2Å, 3.8Å, 3.2Å, and 2.3Å. These values are very close to those observed for the precipitated/molded, undegraded films discussed above, except that the small peak corresponding to 2.8Å was not noticed in either the degraded or unprecipitated samples. The results indicate that neither precipitation nor degradation (to the degree that the sample is brownish in color) causes any significant change in crystal structure for the syndio component. The degradation reduces polymer chain length, as was observed in GPC data for degraded PBD, but not to a point where the characteristic crystal structure changed. With unprecipitated trans samples, 2θ peaks appeared at 20.2°, 22.4°, and 39.0°, which convert to d-spacings of 4.4Å, 4.0Å, and 2.3Å, where the peak at 20.2° (4.4Å) was broad and small and corresponds to the broad amorphous peak observed in the mix cis/trans spectra. As anticipated, these data indicate that no change in crystal structure occurs due to precipitation of trans.

Percent crystallinity for homopolymers was calculated as the ratio of the crystalline peak areas to the total peak area for a given sample, where crystalline peak area is defined as the total peak area minus the amorphous peak area. Precipitated/molded syndio had an overall crystallinity of 51±3% and unprecipitated, molded syndio had a crystallinity of 52±1%. On the other hand, precipitated/molded trans had a crystallinity of 66±1% while unprecipitated, molded trans was 61±2% crystalline. DSC crystallinity calculations on these homopolymers (Marx and Cohen, 1988, ONR Report) gave 41±4% for spincast syndio samples cooled at -200°C/min from the melt and 49±5% for trans crystallized under identical conditions. DSC data from this

report showed precipitated syndio to be 38% crystalline when cooled at 200°C/min to 25°C from the melt while trans was 50% crystalline. In all cases, trans crystallized to a significantly greater extent than the syndio.

Regarding data for the blends, 2θ WAXS scans showed peaks from both of our homopolymers with peak areas for a given component reflecting the proportion of that component in the sample. As with the DSC and rheovibron data, the WAXS blend data once again indicate that blending of 1,2 syndio and 1,4 trans PBDs does not yield an isomorphic structure.

ANALYSIS OF BINARY BLEND MELTS

Light Microscopy

A Nikon Optiphot-pol Polarizing Microscope with a Polaroid 4x5 Land film attachment was employed in conjunction with a Mettler FP 82 Hot Stage to moniter the process of melting in binary blends and to determine whether or not phase separation in the melt phase can be observed. If heterogeneous melts are present it may be possible to observe a transition from heterogeneity to homogeneity (UCST) and to examine at a given temperature the time dependency of the heterogeneous structure of the melt.

Thin flakes of 50/50 blends were heated from room temperature to about 300°C at a rate of 6°C/min. All traces of crystallinity disappeared at ~195°C. Photographs were taken at intervals of about 15-30°C using either the 4X or the 40X objective lenses. Syndio and trans homopolymers were treated in the same way to obtain control information. Most photographs were taken with the polarizing filters aligned at 0°C-10°C to give maximum contrast between crystalline and noncrystalline material in the samples.

In order to test for the effect of time on degree of phase separation, two sets of photographs were taken: one set for a precipitated 50/50 blend that had no additional thermal history and one set for a precipitated 50/50 blend that had been compression molded at 200°C for 2.75 minutes.

With the homopolymers, transmission of polarized light through crystallized regions was relatively uniform until the homopolymer melting point was approached, at which time, the crystallinity faded away from the edges of the sample toward the center until only a completely dark field remained after complete melting was achieved.

For both the molded and unmolded blends, we saw two distinct melting temperature ranges in a 50/50 blend: the first from 120°-

140°C where the trans component melted, and the second from 175°-190°C where the syndio melted. These transitions are characterized by abrupt changes in the transmission of light through the sample. Between the two melting ranges, bright crystallized syndio areas of size 300-700μ were interspersed with dark melted trans areas of 100-400μ, as shown in Figure 12, a photograph of the blend at 160°C under 40X magnification taken with the 4X objective lens. Thus once again we have witnessed separate transitions due to the contributions of the individual components in the blend. No difference in degree of heterogeneity was obvious between the molded and unmolded samples in these temperature ranges.

Once the syndio portions melted, there was no contrast that allowed us to distinguish between what may have been syndio melt areas as opposed to trans melt areas. Furthermore, we did not observe any obvious change of properties as the melted sample was heated far above the melting point, except that the light intensity steadily decreased due to the development of degradation in the sample. Therefore we were unsuccessful in our attempt to determine an UCST. Another possibility is that the blend components may mix in a homogeneous fashion as soon as complete melting is achieved.

In summary, light microscopy showed the presence of distinct domains of syndio and trans in the blends approached the melt phase. We have not yet determined if the melt is initially heterogeneous and if there is an UCST. How time affects heterogeneity and at what point an equilibrium morphology is reached for heterogeneous blends at a given temperature are also open questions at present. Therefore, the next major thrust of our work will be to understand binary blend morphology in the melt.

Ongoing Work and Future Plans

We plan on carrying out a number of light microscopy experiments to answer the questions posed above. Because important changes with time and temperature may be subtle and occur in short periods of time, the polaroid camera is not sufficient for obtaining reliable data. In order to moniter our materials successfully, we will use both 35mm and video cameras. To locate a possible UCST, we will moniter light intensity of a pool of melt as a function of temperature and check if there is an abrupt change in the transmission of light through the melt at a particular temperature. Also, experiments involving quick crystallization of the melt may indicate the degree of heterogeniety in the melt and allow us to measure approximate areas of components in the melt, if the melt is heterogeneous. If successful, this type of experiment can also give us information about the effect of time on heterogeneity.

Mechanical spectrometry will also be used to search for an UCST and determine the degree of heterogeneity at a given temperature as a function of time. Thermal transitions such as UCSTs have been observed in plots of log G' as a function of temperature for a range of frequencies (Cohen and Ramos, 1979). The Rheometrics mechanical spectrometer (Model RMS 800) allows us to work in a nitrogen atmosphere to protect our PBD from oxidation at high temperatures.

Once we have a better idea of what occurs in a melt blend of our homopolymers, we will introduce 1,2/1,4 amorphous PBD diblocks to see if they have an effect on the degree of heterogeneity of the blends. If the effects are advantageous ones, we will also moniter crystallization of the blends in the presence of the diblocks and the room temperature mechanical properties of these modified blends.

SUMMARY OF RESULTS AND CONCLUSIONS

1. Film preparation by solution precipitation followed by compression molding was optimized as an alternative to spin-casting.

2. Avrami analysis indicated that trans began to crystallize at an undercooling of 12.6°C when the DSC cooling rate was 2°/min for two samples with melting points of 132.5° and 132.6°C and syndio began to crystallize at an undercooling of 24.4°C for two samples with melting points of 184.4° and 188.3°C.

3. In isothermally crystallized blends of various compositions of syndio and trans,
   a) distinct melting peaks for both components were observed indicating the absence of isomorphism,
   b) crystallization temperature had no significant effect on the resulting melting temperature for a given composition, and
   c) between the 95/5 blend and trans homopolymer, there was a trans melting point difference of 9°C, while there was only a 2°C difference between the syndio melting points for the 5/95 blend and syndio homopolymer. Also, percent enthalpy data showed that trans is more affected by the presence of the syndio than vice-versa.

4. Rheovibron data showed
   a) a T_g for trans of about -80°C and a T_g for syndio around 25°C,
   b) as with the DSC results, in blends, distinct peaks for both components were present, and
   c) and that the T_g of trans increased with increasing syndio content while the T_g of syndio remained relatively constant.

5. WAXS also showed the presence of distinct peaks for both components in blends. Additionally, WAXS data for precipitated homopolymers gave crystallinities of 51% for syndio and 63% for trans. These values are higher than DSC-determined crystallinity values for similar samples of syndio and trans for which syndio crystallinity was 38% and trans was 50%.

6. Melting of 50/50 blend was observed with a light microscope. Distinct melting of both components was obvious: trans melted between 120° and 140°C and syndio melted between 175° and 190°C. At temperatures between these melting ranges, oval syndio regions were apparent and ranged from 300-700μ in width separated by trans regions of 100-400μ.

7. Future work will involve light microscopy and mechanical spectrometry to determine the degree of heterogeneity of our blends in the melt phase.

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List of Tables and Figures

TABLE 1: RESULTS OF ANTIOXIDANT STUDY

sample	onset of degradation (oC)	melting point (oC)
trans	230	131
trans + 1% ethanox 330	240	132
trans + 1% irganox 1076	255	130
trans + 1% wytox HPM	229	130
syndio	210	186
syndio + 1% ethanox	222	186
syndio + 1% irganox	211	186
syndio + 1% wytox	207	186
syndio	212	185
syndio + 1% ethanox	204	184
syndio + ethanox 2X	216	186
syndio + 1% irganox	216	189
syndio + irganox 2X	237	170

Note: 1% antioxidant is per gram polymer.
2X indicates 1% antioxidant per gram polymer in the tetralin solution in addition to antioxidant in the MeOH to the point of saturation.

TABLE 5a: WAXS DATA

sample	2-theta	d (A)	planes
syndio	13.4	6.6	(010)
(precip)	16.1	5.5	(200),(110)
	21.1	4.2	(210)
	23.4	3.8	(111),(201)
	28.0	3.2	(120),(310)
	31.6	2.8	(021),(220)
	35.9	2.5	(102),(221)
trans	22.4	4.0	(100)
(precip)	39.1	2.3	(110)
1,4 amorphous	19.6	4.5	

syndio in lit:
Natta/Corradini (1956): d = 6.6, 5.5, 4.2, 3.8

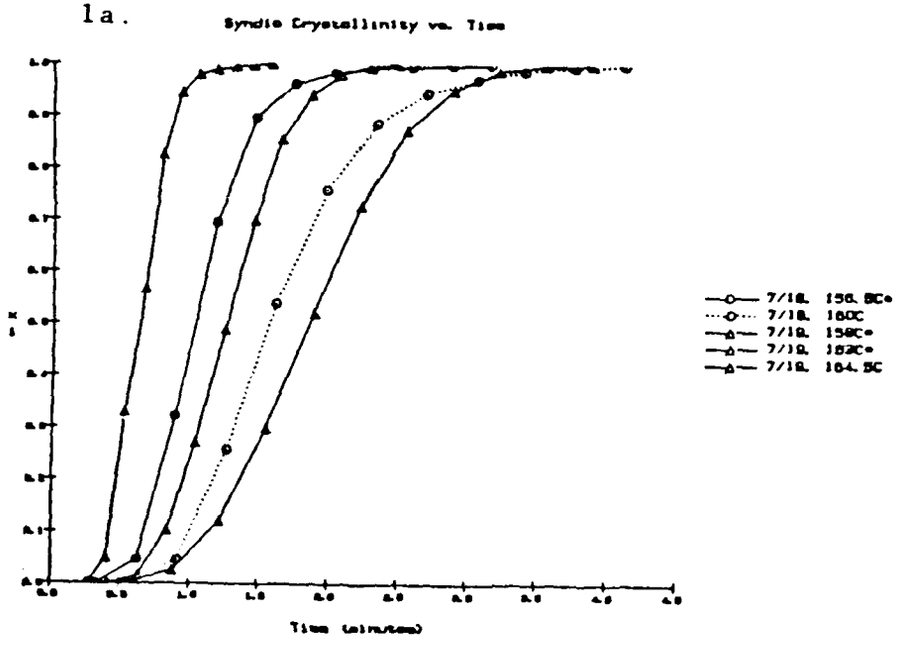
trans in lit:
Natta (1962), Iwayanagi et al. (1968): peak at = 22.6
Bermudez and Fatou (1972): peak at 22.5, (100)

TABLE 5b: UNIT CELL DIMENSIONS

Sample	Source	Cell Type	Dimensions (A)		
syndio	Natta/Corradini (1956)	orthorhombic	a=10.98	b=6.60	c=5.14
trans	Iwayanagi et al. (1968)	monoclinic	a= 8.63	b=9.11	c=4.83
(mod I)	Natta/Corradini (1959)	hexagonal	a= 4.54		c=4.92
	Seuhiro/Takayanagi (1970)	hexagonal	a= 4.60		c=4.83
trans	Natta/Corradini (1959)	hexagonal	a= 4.88		c=4.68
(mod II)	Seuhiro/Takayanagi (1970)	hexagonal	a= 4.95		c=4.66

Figure 1: Homopolymer Isothermal Crystallization vs. Time

1a.



1b.

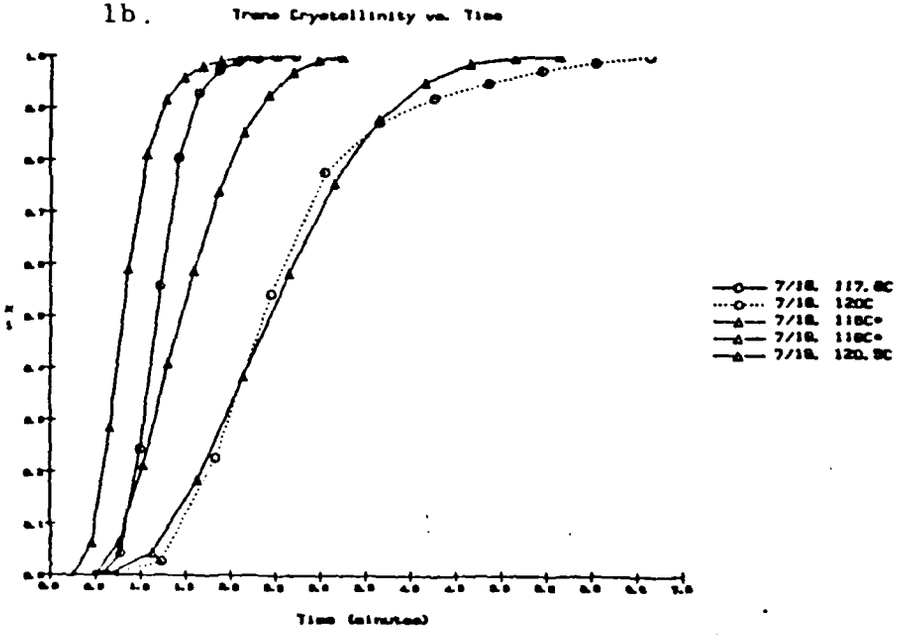


Figure 2: Homopolymer Avrami Plots

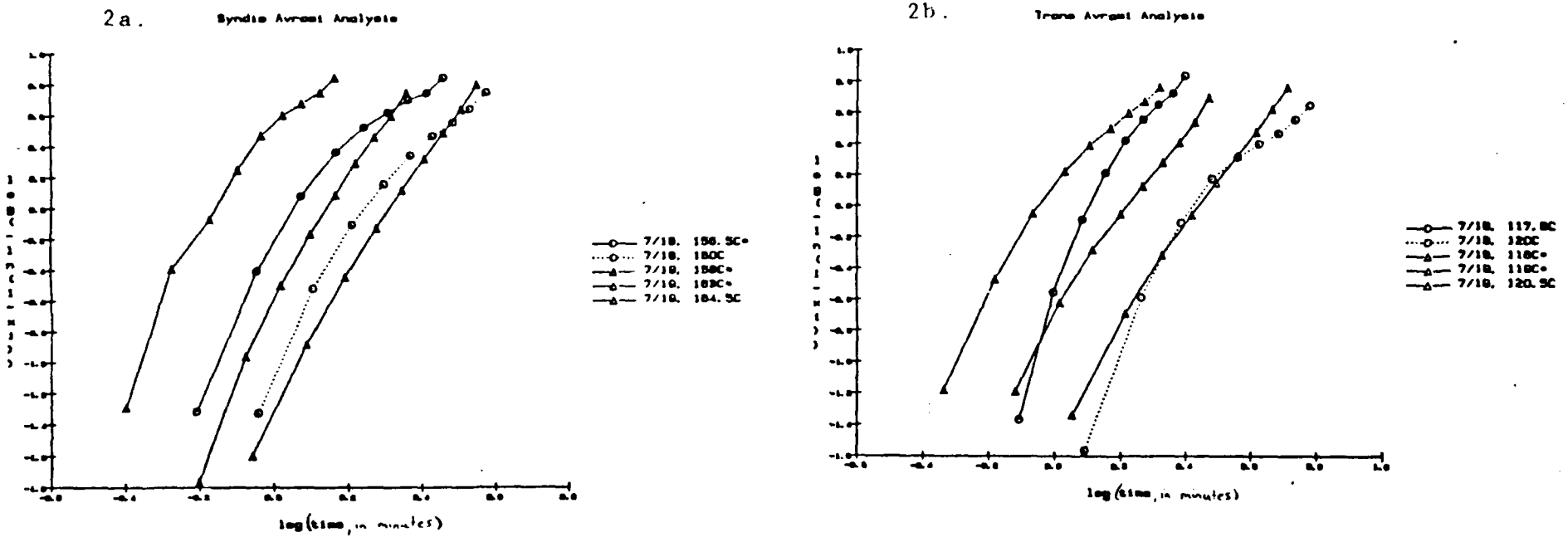


Table 2: Avrami Constants for Trans and Syndio Homopolymers

# and sample	melt T	cryst T	undercool	n short	log k short	n long	log k long	n avg	log k avg	k avg
1. 7/18 trans	132.6	117.8	14.8	6.77	-0.60	2.13	-0.02	4.45	-0.31	0.49
2. 7/18 trans	132.6	120.0	12.6	4.95	-1.96	1.48	-0.52	3.21	-1.24	0.06
5. 7/19 trans	132.5	116.0	16.5	4.14	0.23	1.74	0.21	2.94	0.22	1.67
6. 7/19 trans	132.5	119.0	13.5	3.86	-0.70	2.77	-0.63	3.32	-0.67	0.22
7. 7/19 trans	132.5	120.5	12.0	3.73	-1.52	2.85	-1.27	3.29	-1.40	0.04
3. 7/18 syndio	184.4	156.5	27.9	4.94	-0.25	1.47	0.16	3.21	-0.04	0.90
4. 7/18 syndio	184.4	160.0	24.4	4.86	-1.09	1.89	-0.36	3.38	-0.73	0.19
8. 7/19 syndio	188.3	158.0	30.3	5.59	0.99	1.85	0.53	3.72	0.76	5.76
9. 7/19 syndio	188.3	163.0	25.3	5.78	-0.57	3.35	-0.46	4.56	-0.52	0.30
10. 7/19 syndio	188.3	164.0	24.3	4.69	-1.33	3.30	-1.03	4.00	-1.18	0.07

Figure 3: k(avg) vs. Undercooling

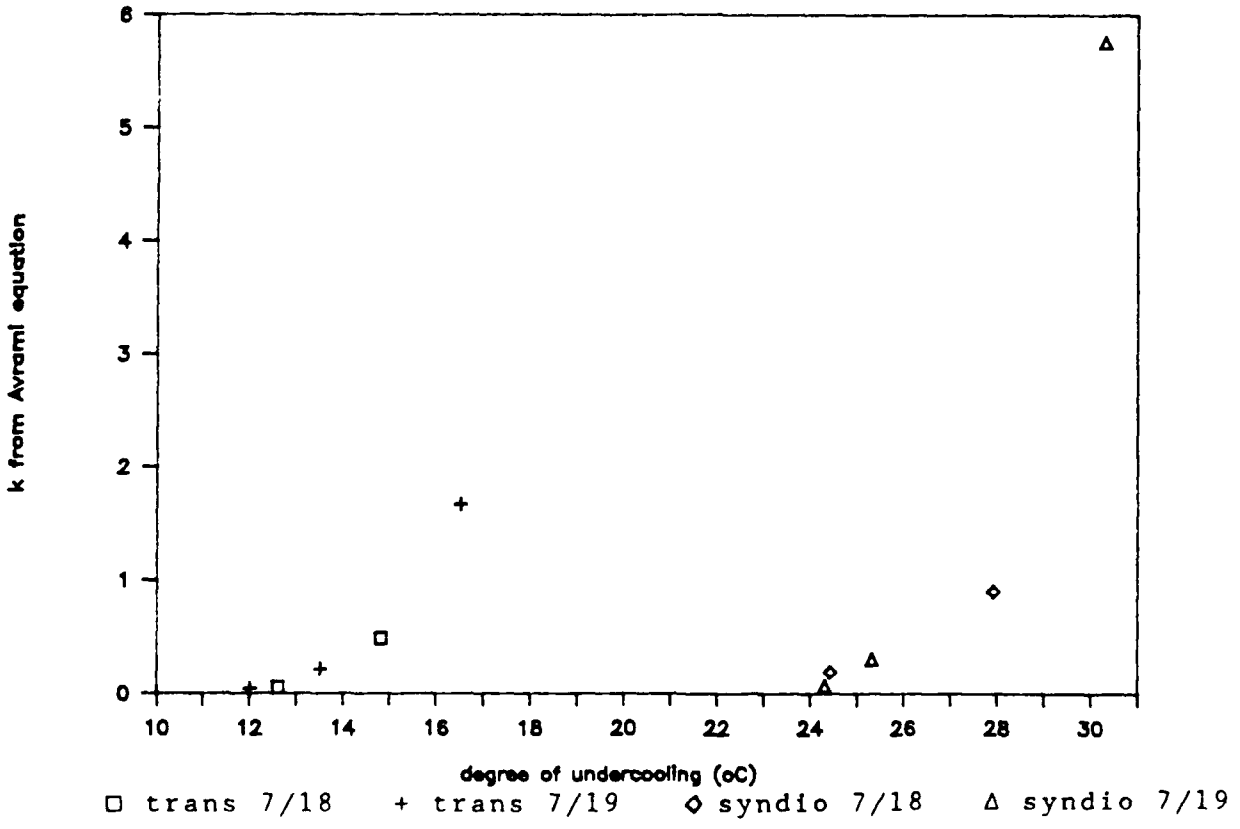


TABLE 3: EFFECT OF COMPOSITION AND TEMPERATURE ON BLENDS

date	d(ind)* [oC]	blend	iso T [oC]	Ttl [oC]	TtII [oC]	Ts [oC]	Htl [cal/g]	HtII [cal/g]	Hs [cal/g]	%HtI**	%HtII**	%Hs**
7/8***	0.6	100/ 0	165			187.9			9.3			100.0
8/22	0.0	95/ 5	165	69.0	124.2	189.0	0.7	0.1	9.1	3.4	1.6	97.5
8/23	1.1	75/25	165	67.8	124.6	186.6	4.5	1.8	7.0	22.3	19.9	75.7
7/8	0.6	50/50	165	72.9	132.4	188.0	9.9	4.1	5.0	49.5	47.2	53.4
8/23	1.1	25/75	165	71.3	130.1	186.7	14.9	6.5	2.6	74.8	74.4	27.6
8/22	0.0	5/95	165	73.8	133.4	185.5	19.8	8.6	0.7	99.3	97.9	7.3
7/8	0.6	0/100	165	71.3	132.6		19.9	8.8		100.0	100.0	
8/8	0.9	100/ 0	155			187.2			9.1			100.0
8/8	0.9	50/50	155	74.4	133.4	188.1	10.2	4.3	5.0	50.0	51.8	54.2
8/8	0.9	0/100	155	71.1	132.1		20.3	8.3		100.0	100.0	
8/8	0.9	100/ 0	140			185.7			9.3			100.0
8/22	0.0	95/ 5	140	69.0	124.7	187.8	0.8	0.2	9.2	3.7	2.9	99.5
8/23	1.1	75/25	140	69.0	125.5	186.2	4.5	1.8	7.1	22.2	21.8	76.5
8/8	0.9	50/50	140	75.0	133.8	188.4	9.9	4.1	5.1	48.6	49.6	54.9
8/23	1.1	25/75	140	70.2	129.3	186.3	15.8	7.2	2.9	77.6	86.6	31.2
8/22	0.0	5/95	140	75.0	135.3	185.1	19.5	8.5	0.7	95.7	102.2	7.2
8/8	0.9	0/100	140	71.4	132.5		20.4	8.3		100.0	100.0	
9/1	0.5	5/95	140	75.4	134.6	186.7	20.1	8.9	0.8			
8/8	0.9	100/ 0	125			186.6			9.2			100.0
8/8	0.9	50/50	125	73.2	132.5	187.3	10.3	4.5	5.0	51.2	54.5	53.9
8/8	0.9	0/100	125	71.5	132.8		20.0	8.3		100.0	100.0	
8/8	0.9	100/ 0	110			186.3			9.4			100.0
8/8	0.9	50/50	110	73.0	132.6	186.7	10.5	4.6	4.8	50.8	54.8	51.3
8/8	0.9	0/100	110	72.2	133.0		20.7	8.3		100.0	100.0	
7/8	0.6	100/ 0	25			186.7			9.3			100.0
7/8	0.6	50/50	25	73.9	133.3	188.0	10.3	4.4	4.8	50.8	48.7	51.4
7/8	0.6	0/100	25	71.3	132.3		20.2	9.0		100.0	100.0	
8/8	0.9	0/100	25	71.2	132.3		20.4	8.3				
9/28	1.2	100/ 0	-			189.3			17.3			100.0
9/28	1.2	95/ 5	-	69.8	small	189.0	0.2	small	14.0	0.8	small	80.9
9/28	1.2	75/25	-	70.5	126.0	187.6	3.7	1.4	10.8	17.4	13.2	62.1
9/28	1.2	50/50	-	73.0	132.7	189.4	9.5	4.7	8.0	44.9	44.5	46.4
9/28	1.2	25/75	-	67.7	131.0	187.0	13.6	6.5	3.1	64.2	61.5	18.0
9/28	1.2	5/95	-	69.8	136.3	186.9	18.8	10.1	0.6	88.4	96.4	3.3
9/28	1.2	0/100	-	72.1	133.9		21.2	10.5		100.0	100.0	

* d(ind) is the difference between the indium melting point determined on the day of the experiment and 160.5oC
All temperature values are corrected by a value equal to d(ind).

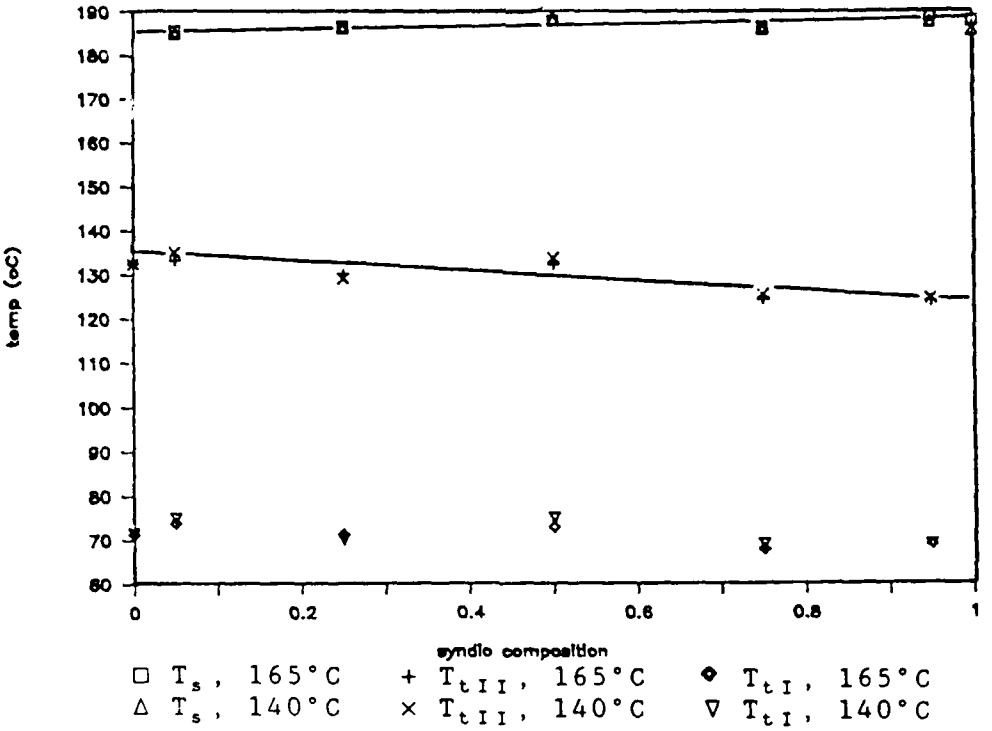
** %H values are the percent enthalpy relative to enthalpy of homopolymer sample.

***No indium standard was run on 7/8 but is assumed here to be 0.6,
as determined by comparing identical runs at 25oC for 7/8 and 8/8.

- indicates samples were heated directly from precipitated state

Figure 4: Blend Isothermal Crystallization Results for 165°C and 140°C Trials

4a. Thermal Transitions as a Function of Syndio Composition



4b. Percent Enthalpy as a Function of Syndio Composition

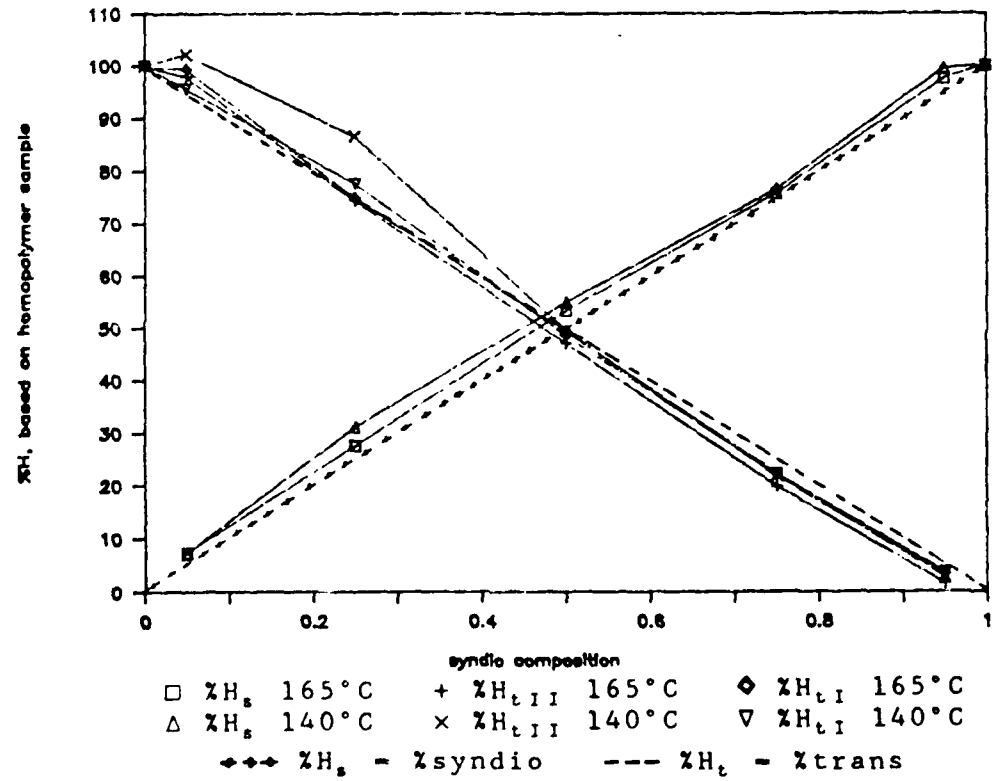
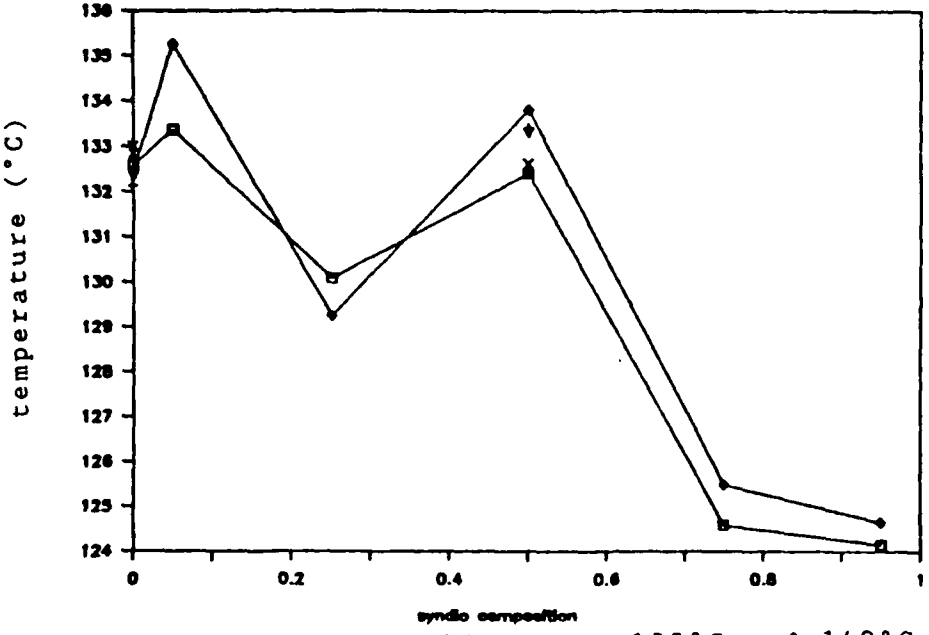


Figure 5: Blend Melting Points for All Temperature Trials

(Expanded Temperature Scale)

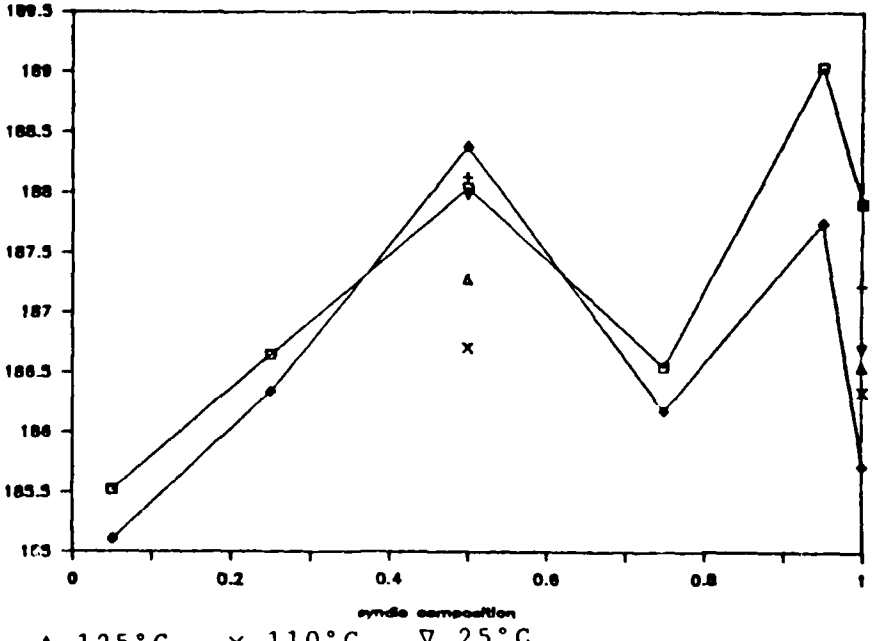
5a. Trans Melting point

as a Function of Syndio Composition



5b. Syndio Melting point

as a Function of Syndio Composition



□ 165°C + 155°C ◇ 140°C Δ 125°C × 110°C ▽ 25°C

Figure 6: Blend Percent Enthalpies for All Temperature Trials

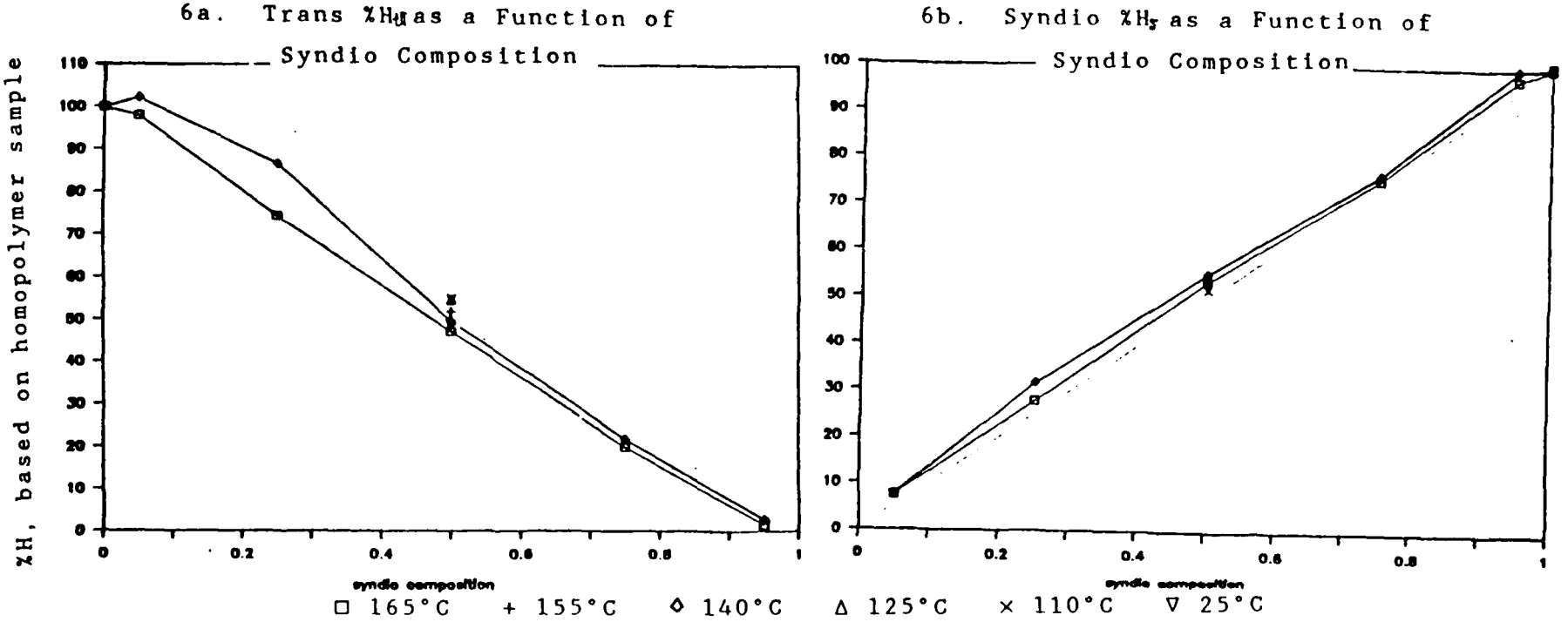
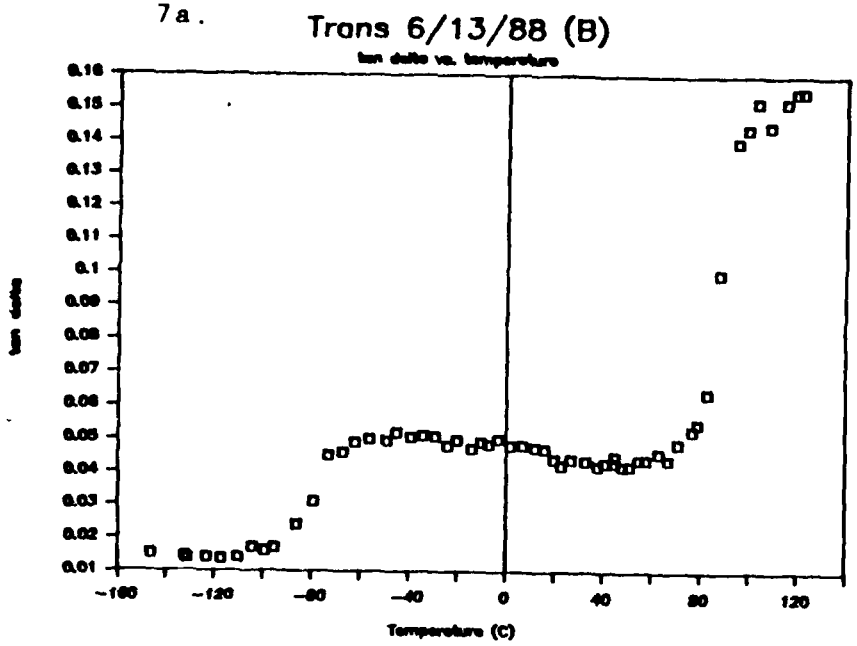
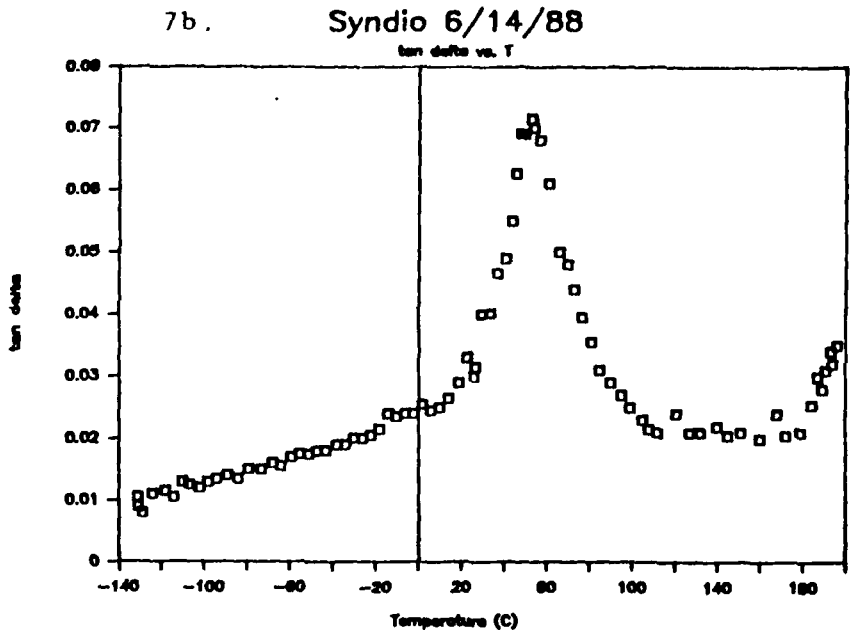


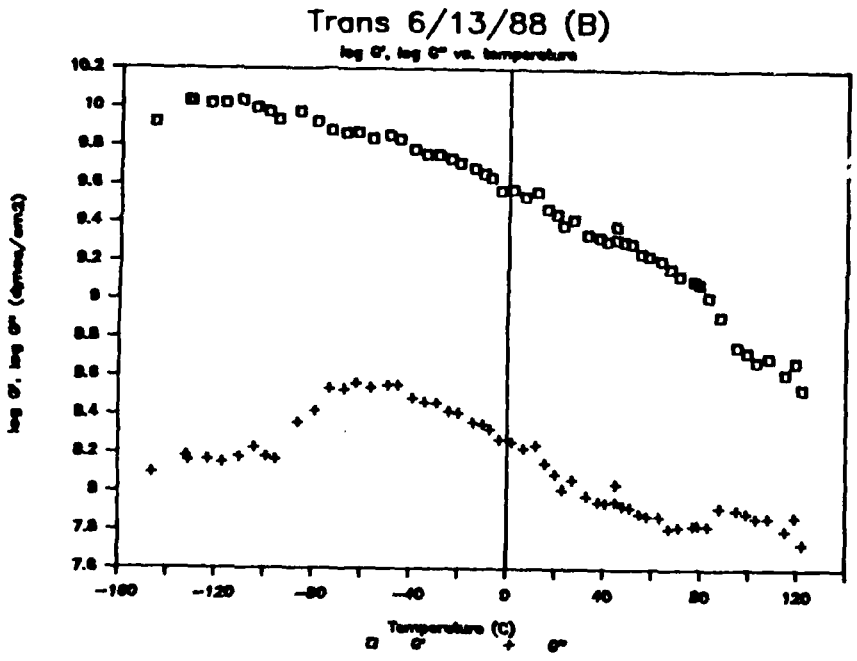
Figure 7: Rheovibron Data for Unprecipitated Homopolymers

7a.



7b.





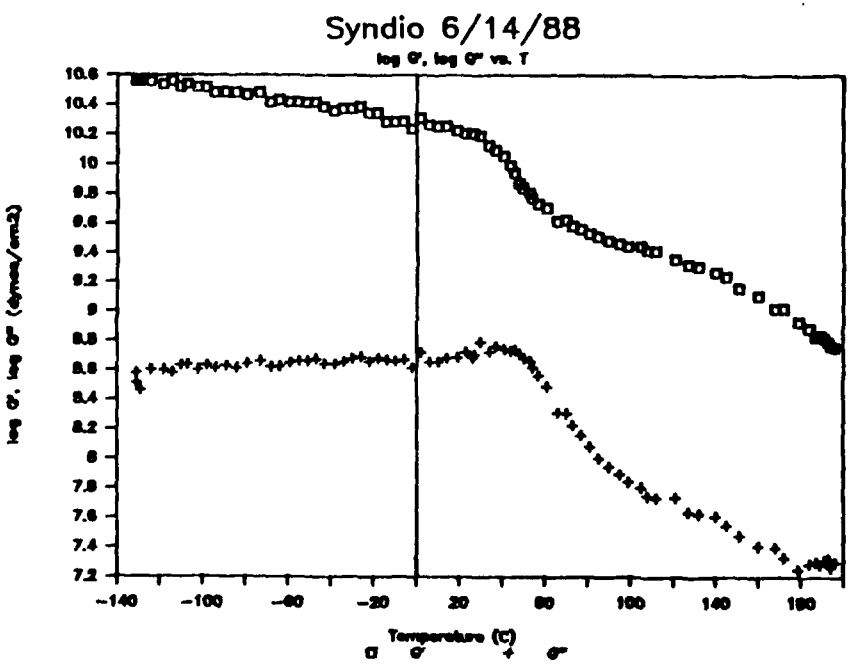
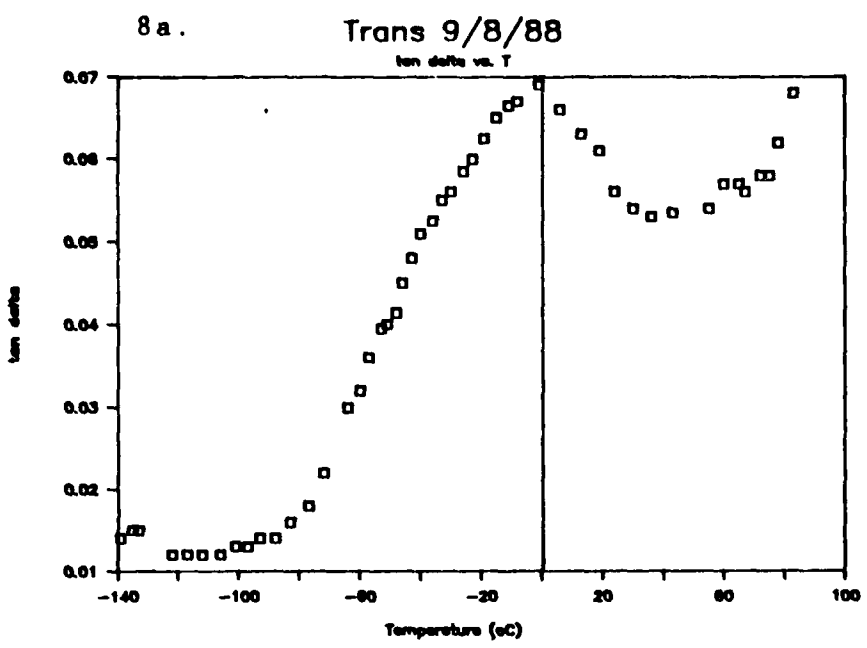
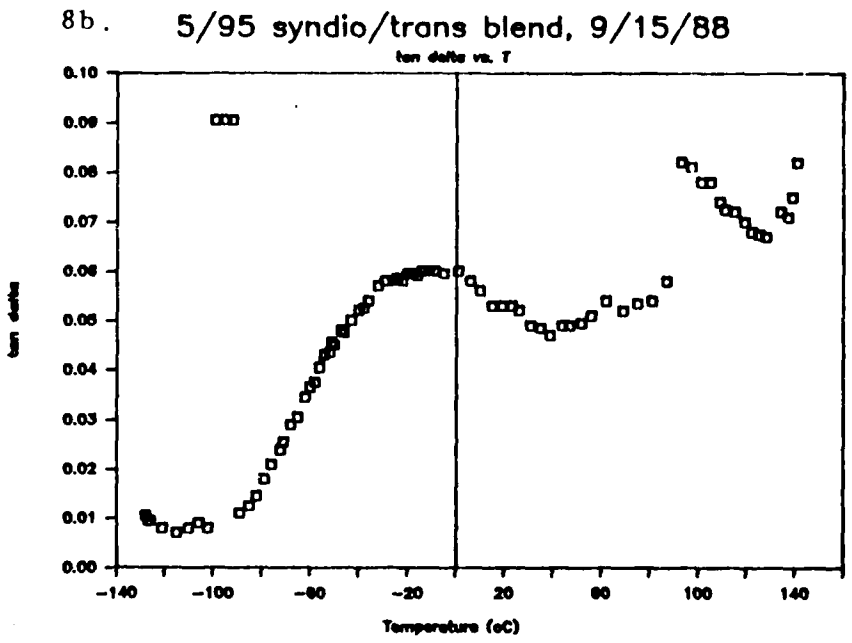


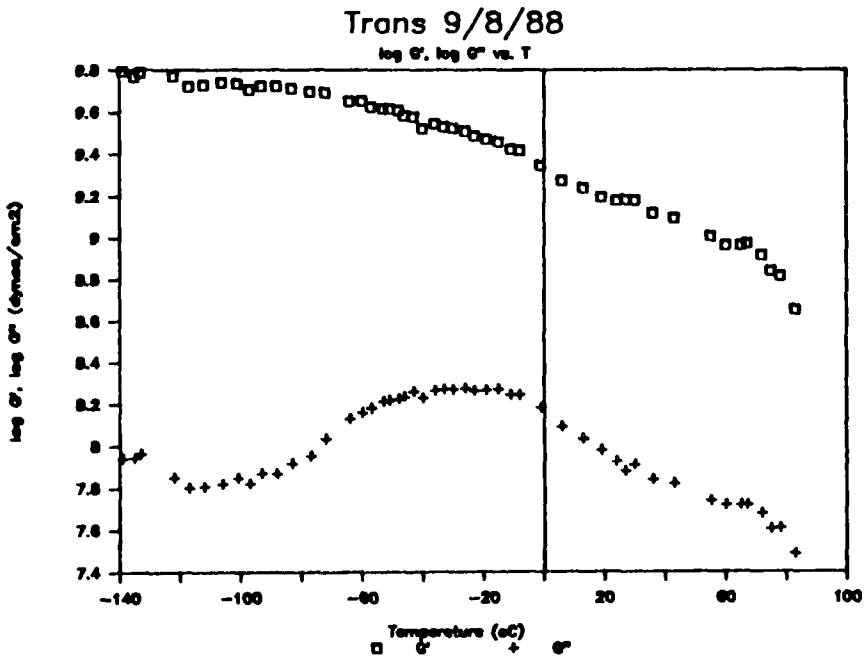
Figure 8: Rheovibron Data for Precipitated Homopolymers and Blends

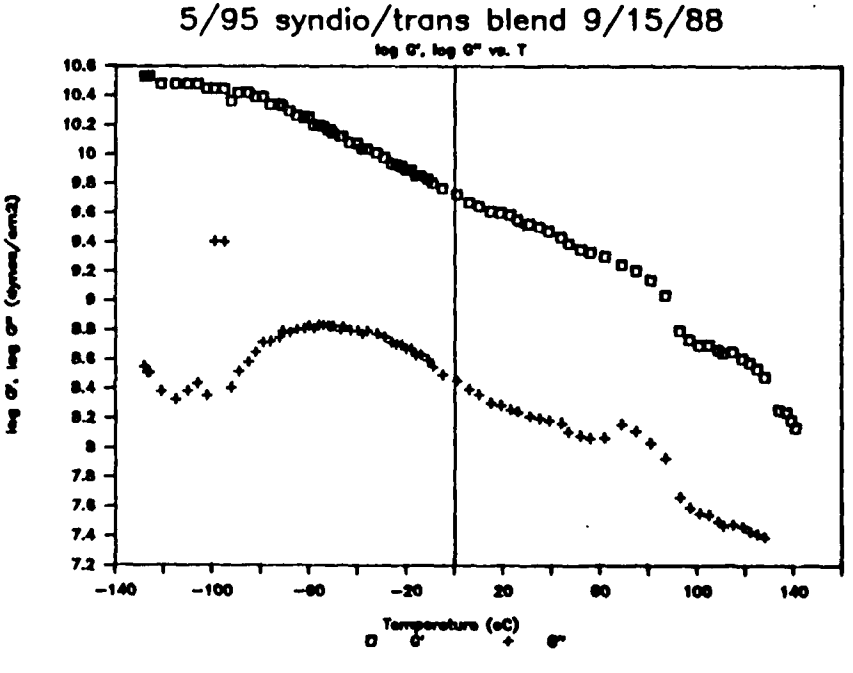
8a.



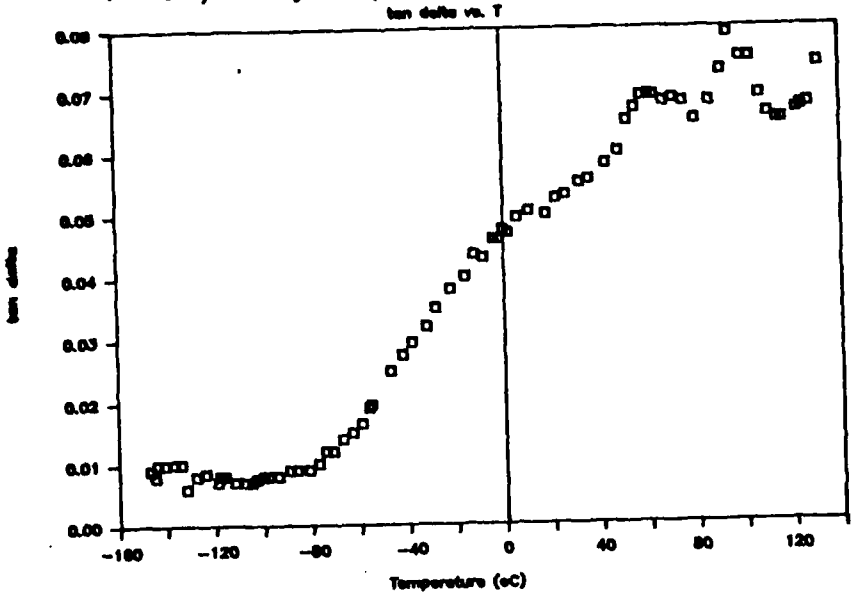
8b.



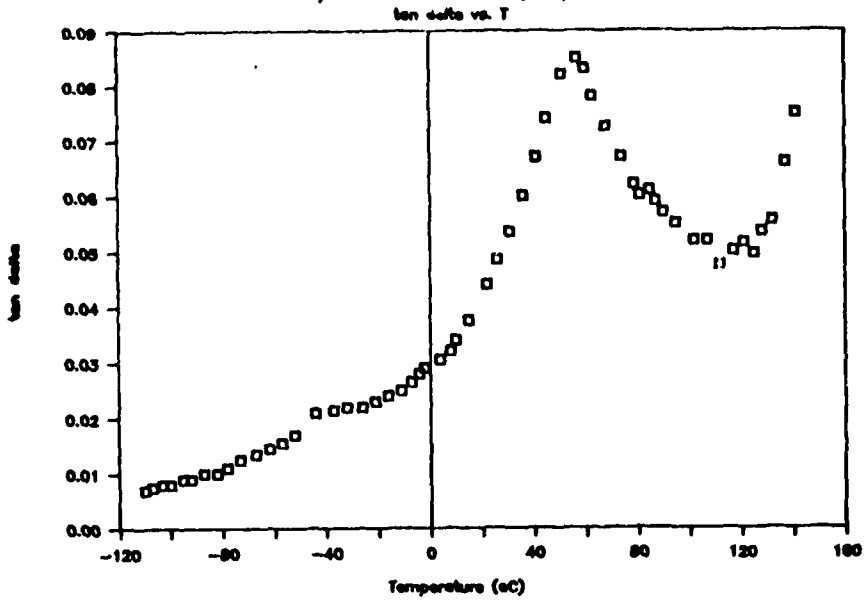




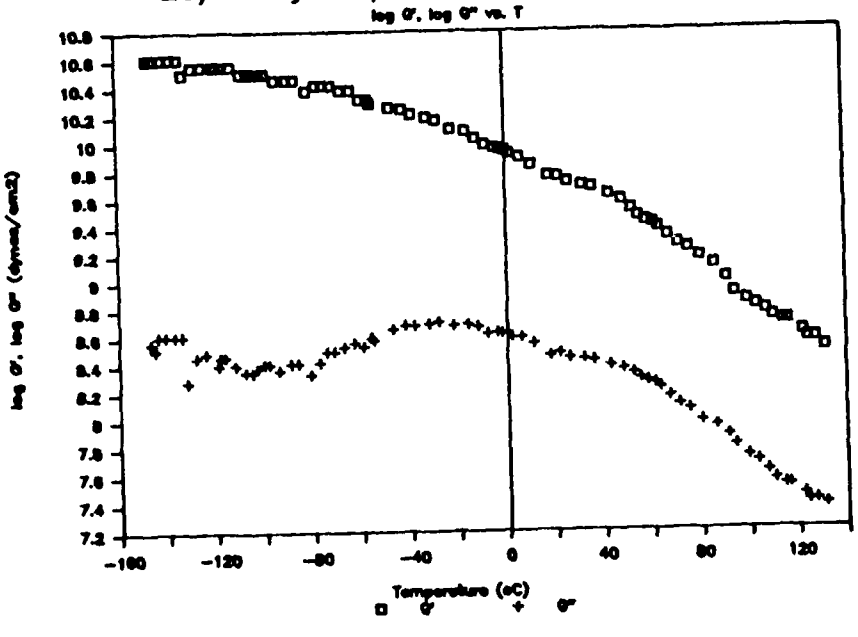
8c. 25/75 syndio/trans blend 9/14/88



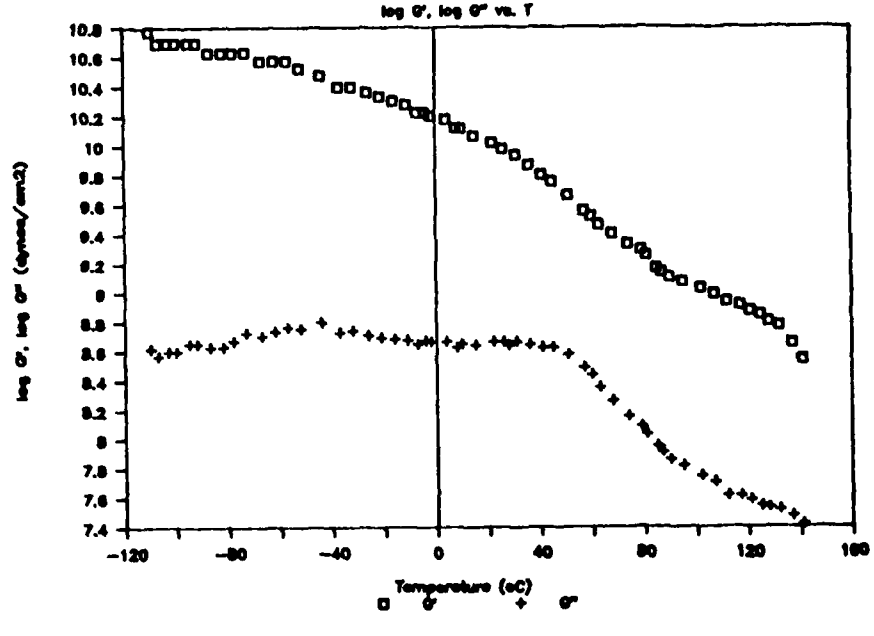
8d. 50/50 blend, 9/8/88



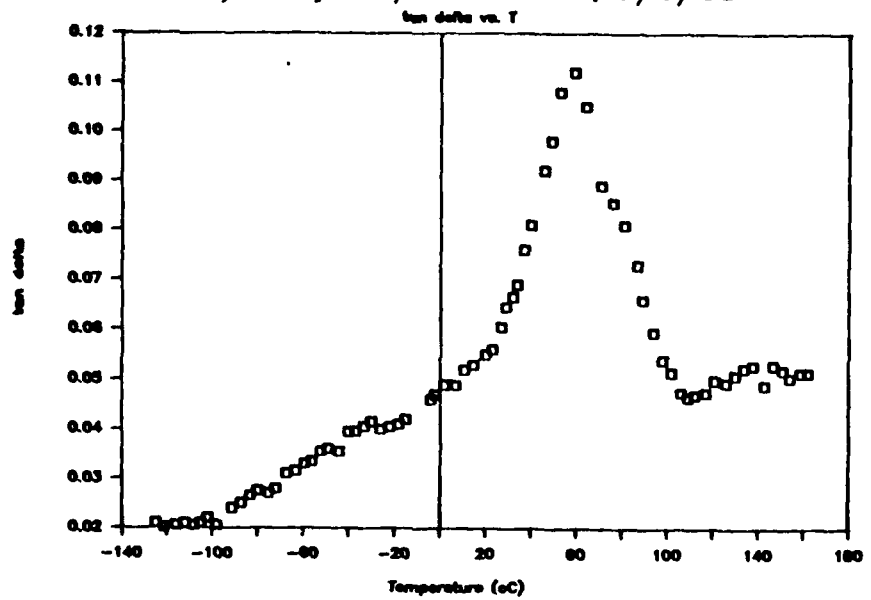
25/75 syndio/trans blend, 9/14/88



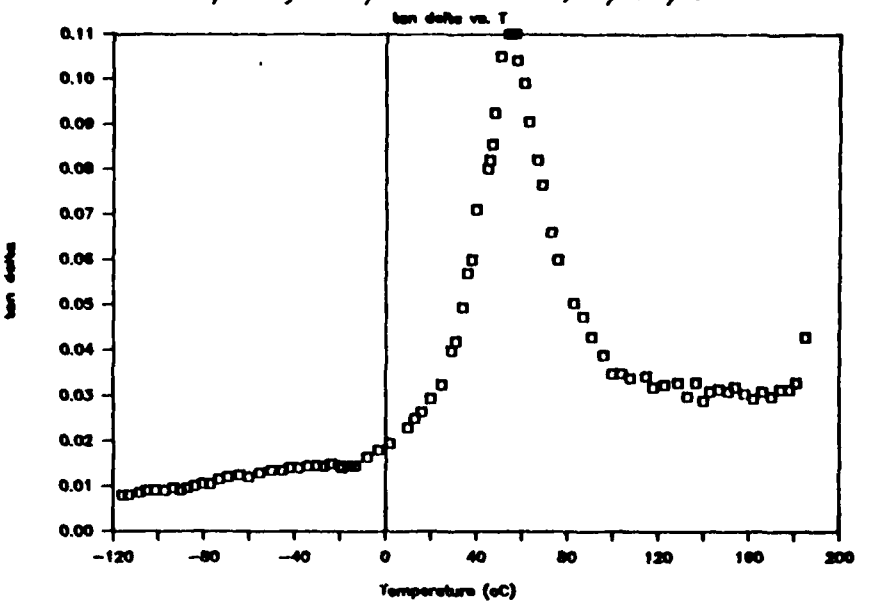
50/50 Blend, 9/8/88



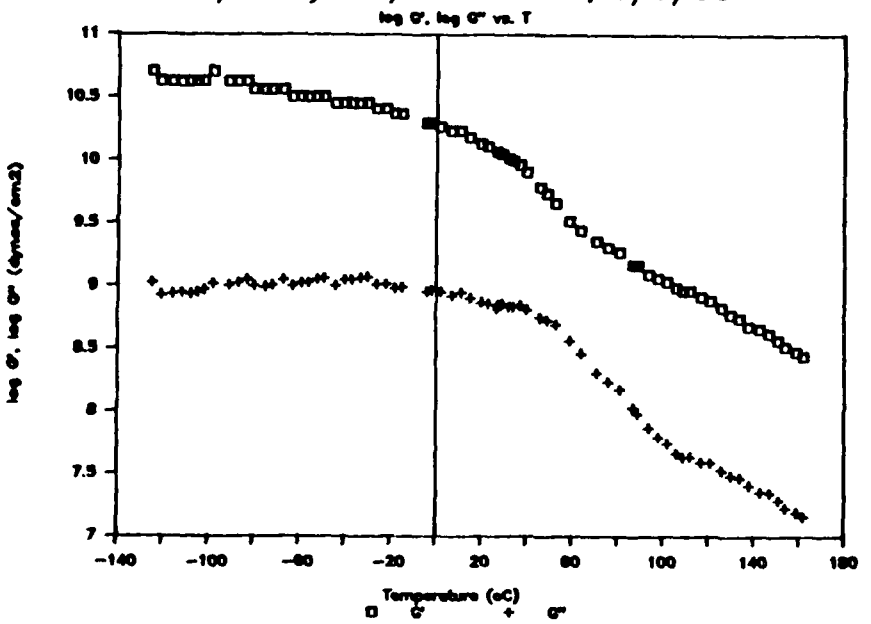
8e. 75/25 syndio/trans blend, 9/8/88



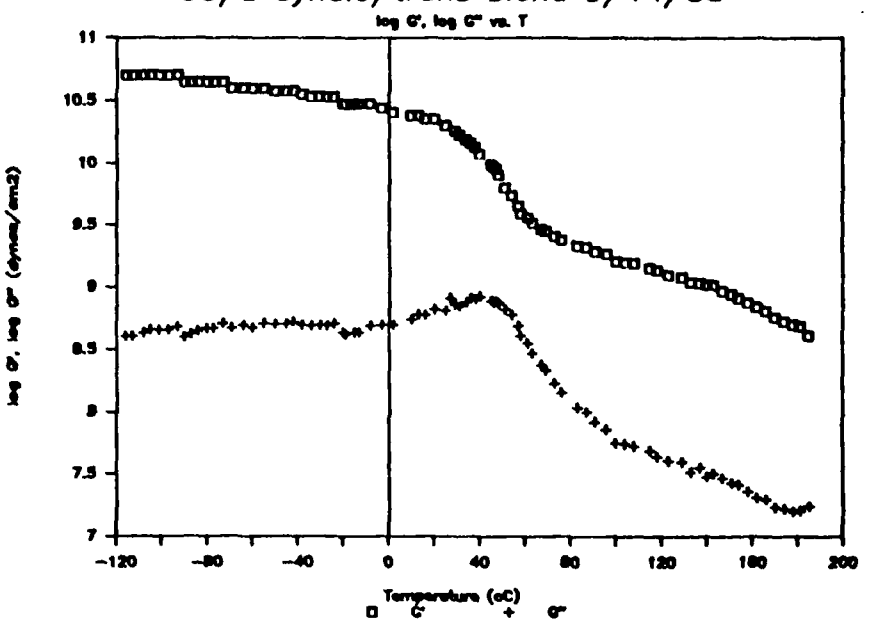
8f. 95/5 syndio/trans blend, 9/14/88



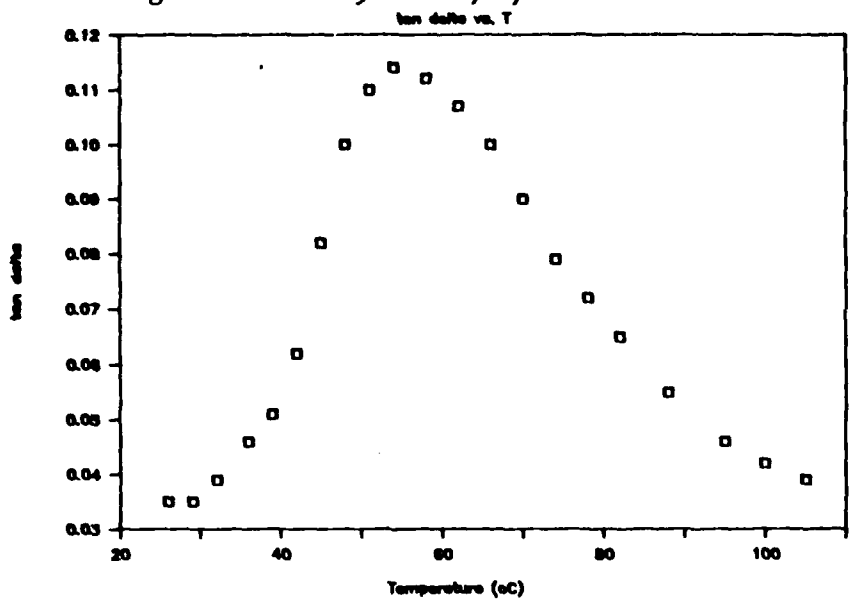
75/25 syndio/trans blend, 9/8/88



95/5 syndio/trans blend 9/14/88



8g.


Syndio 9/7/88
tan delta vs. T
tan delta
0.12
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
20
40
60
80
100
Temperature (oC)

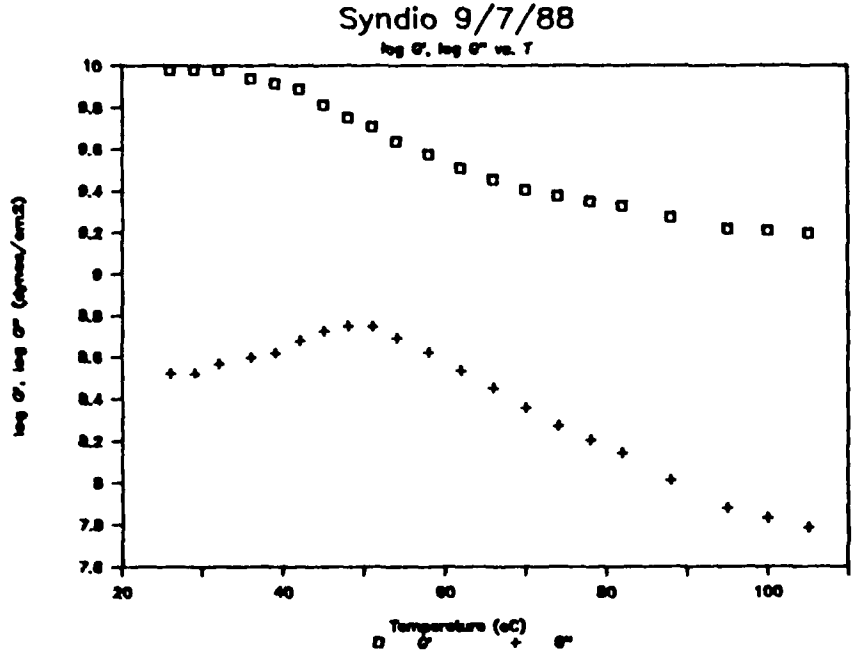
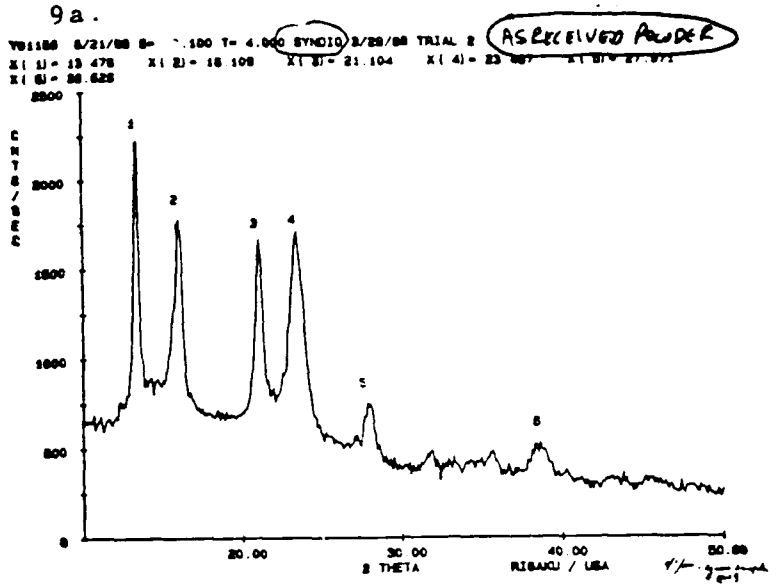

Syndio 9/7/88
log G', log G" vs. T
log G', log G" (dynes/cm2)
10
9.8
9.6
9.4
9.2
9
8.8
8.6
8.4
8.2
8
7.8
7.6
20
40
60
80
100
Temperature (oC)
G'
G"

TABLE 4: TAN DELTA TRANSITIONS IN HOMOPOLYMERS AND BLENDS

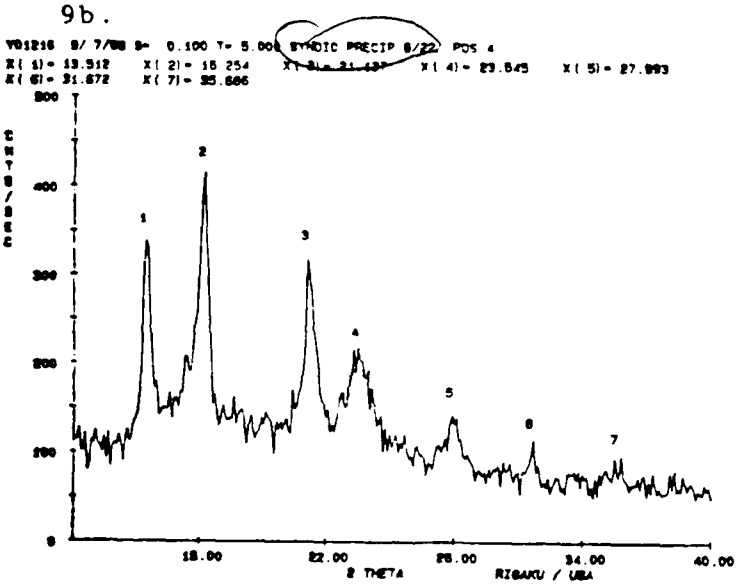
sample	temperature test range (oC)	transition temperatures (oC)
PET 11/22/87	20 - 220	90
PET 9/16/88	-100 - 200	-90, 90
syndio 5/31/88	25 - 195	-20, 185
syndio 6/13/88	35 - 195	-20, 190
syndio 6/14/88	-135 - 200	25, 185
trans 5/31/88	25 - 120	80
trans 6/13/88 A	45 - 120	80
trans 6/13/88 B	-145 - 120	-85, 80
syndio 9/7/88 (precip)	25 - 105	35
trans 9/8/88 (precip)	-140 - 85	-80, 70
5% syndio 9/15/88	-130 - 140	-85, 85, 140
25% syndio 9/14/88	-150 - 130	-70, 30, 85, 130
50% syndio 9/8/88	-110 - 140	-60, 20, 135
75% syndio 9/8/88	-130 - 160	-50, 25, 125
95% syndio 9/14/88	-120 - 185	25, 185

Figure 9: Homopolymer WAXS Scans

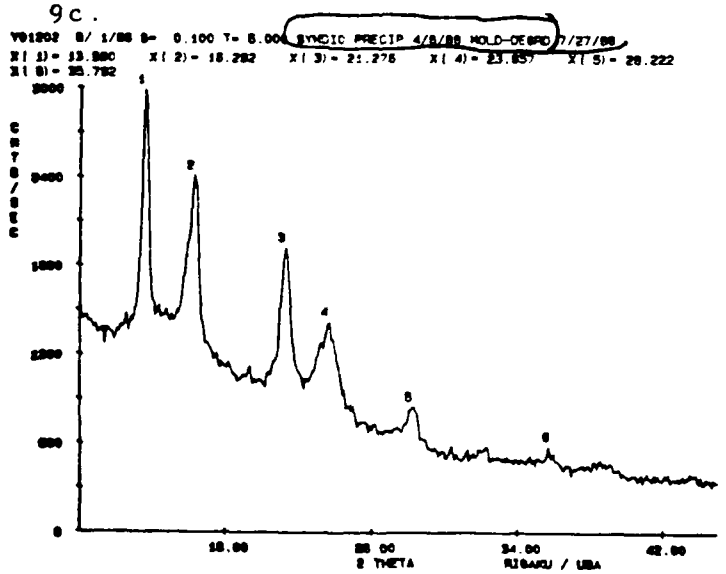
9a.



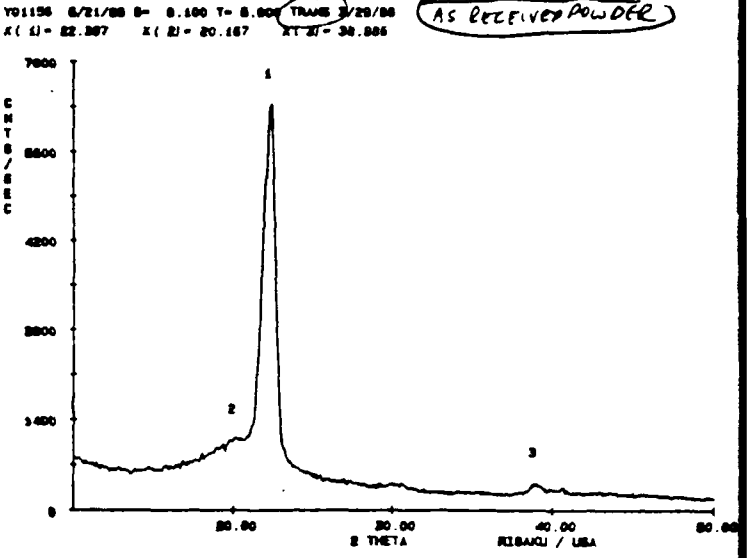
9b.



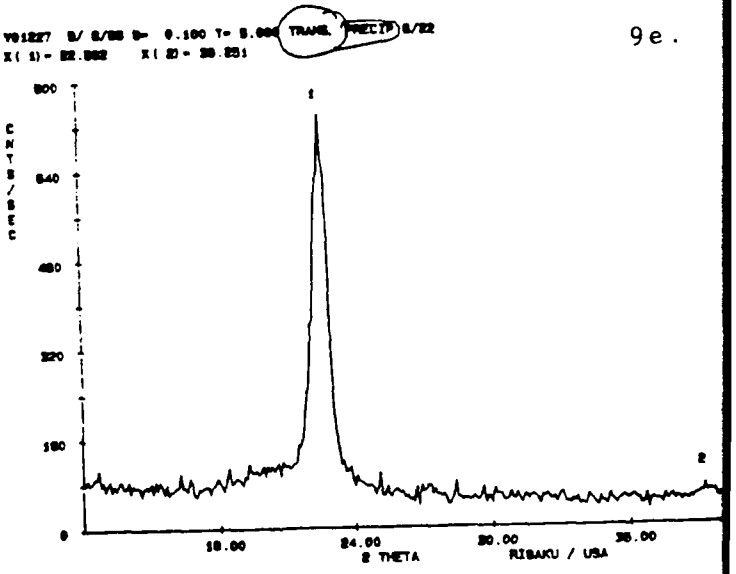
9c.



9d.



9e.



9a. Unprecipitated Syndio

9b. Precipitated Syndio

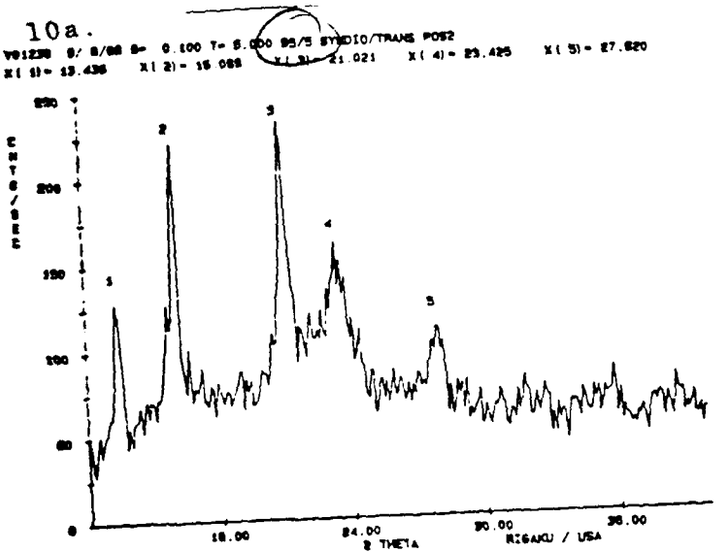
9c. Precipitated Degraded Syndio

9d. Unprecipitated Trans

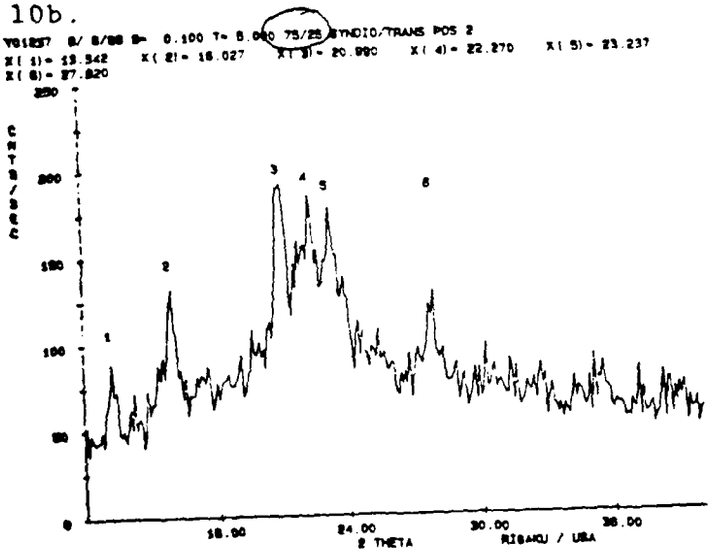
9e. P ecipitated Trans

Figure 10: Blend WAXS Scans

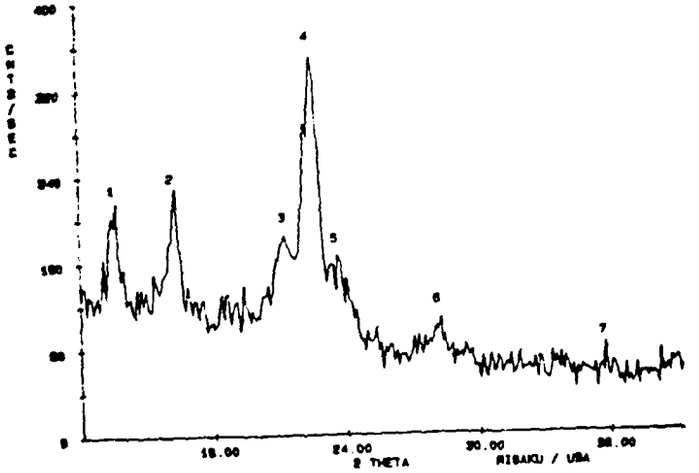
10a.



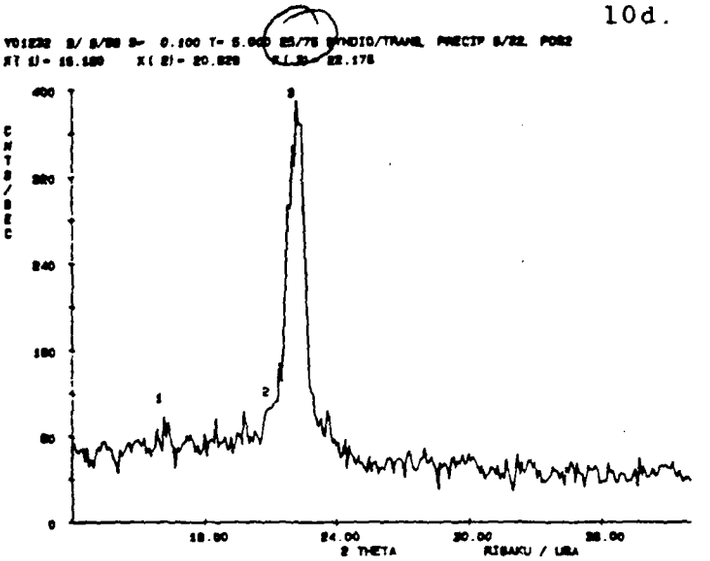
10b.



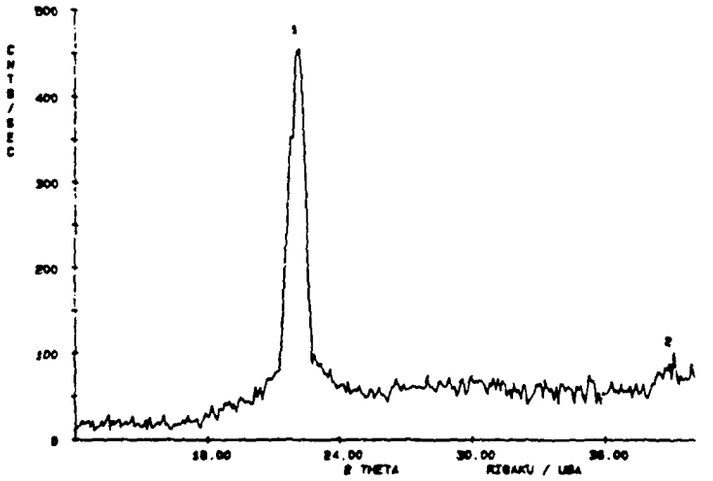
10c.



10d.



10e.



10a. 95/5 (syndio/trans)

10b. 75/25

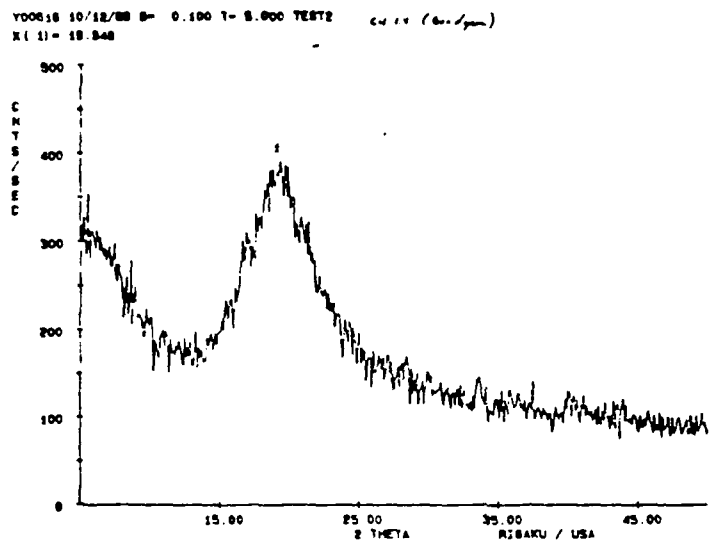
10c. 50/50

10d. 25/75

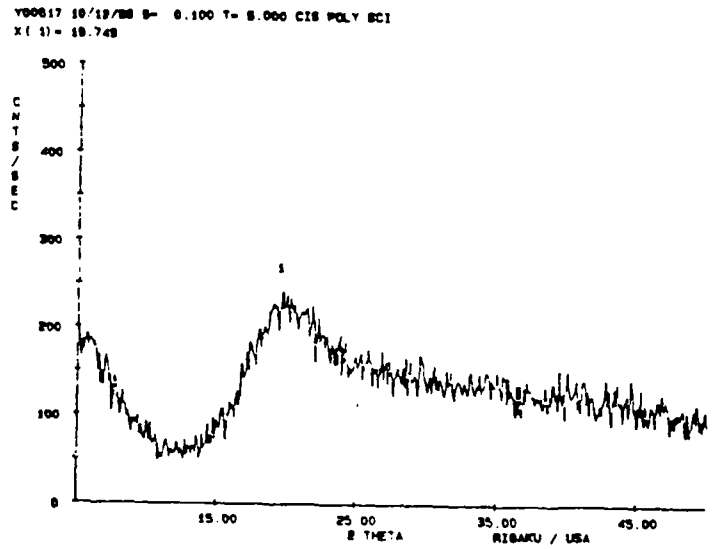
10e. 5/95

Figure 11: WAXS of Amorphous 1,4 PBD

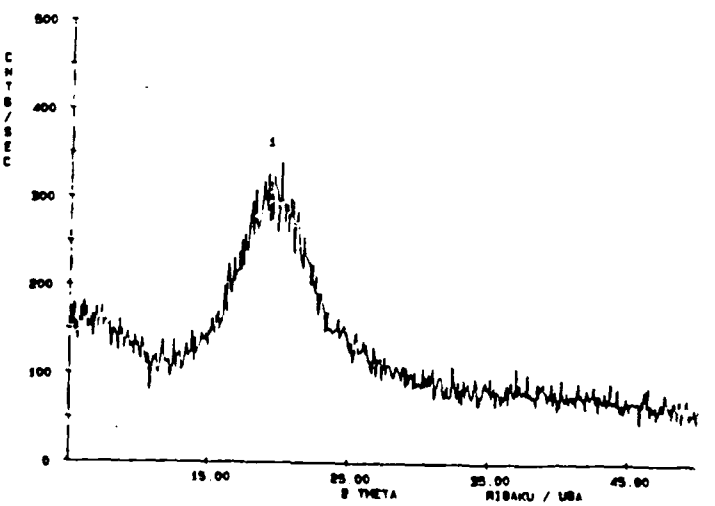
11a.



11b.



11c.



11a. Cis (Goodyear)

11b. Cis (Polysciences)

11c. Cis/Trans Mixed

Figure 12: 50/50 blend (precip/molded)
160°C, cross polarized